



Appendix C

Laboratory Standard Operating Procedures and Quality Assurance

Merit Laboratories, Inc.

1. Quality Assurance Manual
2. VOCs
3. SVOCs
4. PCBs
5. Extractions for SVOCs
6. Extractions for PCBs
7. Metals
8. Metals Digestions for metals
9. Mercury (with digestions)
10. Anions (Chloride, Sulfate, NO₂, NO₃)
11. Hardness
12. Alkalinity
13. Ammonia
14. TDS
15. TOC
16. pH
17. Conductivity
18. Cyanide
19. Turbidity
20. List of SOPs (Prepared By: Merit Laboratories, Inc.)

QUALITY ASSURANCE MANUAL

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1.0 POLICY STATEMENT

- 1.1 This Quality Manual summarizes the policies and operational procedures associated with Merit Laboratories, Inc. (Merit) in East Lansing, MI. Protocols for sample handling and storage, chain-of-custody, laboratory analyses, data reduction, corrective action, and reporting are described or referenced. All policies and procedures have been structured in accordance with the National Environmental Laboratory Accreditation Conference (NELAC) standards adopted in June 2003, Environmental Laboratory Approval Program (ELAP) certification manual updated in August 2009 (current as of the date of this publication) and applicable Environmental Protection Agency (EPA) requirements, regulations, guidance, and technical standards. This manual has been prepared in accordance with the guidance documents listed in Section 15. Further details on these policies and procedures are contained in SOPs and related documents. This Quality Manual, SOPs, and related documentation describe the quality system for Merit.
- 1.2 Merit performs chemical analyses for inorganic and organic constituents in water, soil and waste. Merit's goal is to produce data that is scientifically valid, defensible, and of known and documented quality in accordance with standards developed by the NELAC and any applicable state or EPA regulations or requirements. A Certification Statement (see Appendix A) has been recorded to this effect.
- 1.3 Merit analyzes Proficiency Test (PT) samples multiple times per year. Two times a year Merit participates in a NELAP conducted PT program where certification is suspended for any analyte that receives two out of three consecutive unsatisfactory results. Merit currently uses ERA for the rest of its PT studies, ERA is A2LA and ISO 9001 certified. Merit does two WP studies every year in accordance with its' Ohio VAP certification and a WS PT study once a year in accordance with its' drinking water certification. Merit also posts results for the DMRQA study every year. The specific analytes and matrices analyzed are based on the current scope of the laboratory services. A Certification Summary Table (Appendix N) contains the analytes, method(s), and certification for which Merit holds.
- 1.4 The technical and service requirements of all requests are to provide analyses that are thoroughly evaluated before commitments are made to accept the work. This includes a review of facilities and instrumentation, staffing, and any special QC or reporting requirements to ensure that analyses can be performed within the expected schedule. All measurements are made using the most recently published reference methods or methods developed and validated by Merit. Competence with all methods (for each matrix) is demonstrated using regular quality control samples, MDLs, precision and accuracy studies as well as PT study results.
- 1.5 Merit has developed a proactive program for prevention and detection of improper, unethical or illegal actions. Components of this program include: internal proficiency testing (single and double blind); electronic data audits and post-analysis data review by a second analyst or the QA Officer; and SOPs identifying appropriate laboratory and instrument manipulation practices. Merit holds annual Data Integrity training for all staff.

2.0 ORGANIZATION AND RESPONSIBILITIES

2.1 Organizational Chart

The organizational chart for Merit Laboratories follows in Appendix D. Job descriptions for all individuals are maintained on a secure drive on the company computer system.

Merit has an established a Technical Competence of Staff and Merit Labs Position Descriptions and Responsibilities document. All the positions and back up personnel are cross referenced and outlined in Appendix D after the Organizational Chart.

2.2 Laboratory Director

The Laboratory Director is responsible for:

- 2.2.1 All technical and financial areas of the company

2.2.2 Approval of all laboratory reports and invoices

2.2.3 Defining the minimum level of experience and skill necessary for all positions in the laboratory

2.2.4 Supervising all personnel

2.2.5 Ensuring that outside support and services are of adequate quality to sustain confidence in the laboratory's tests

2.3 Technical Director

The Technical Director is responsible for:

2.3.1 Responsible for Merit's QAS and its implementation

2.3.2 Overall technical functions in the laboratory

2.3.3 Certifying that staff is qualified for their positions

2.3.4 Ensuring there is enough qualified staff to accomplish all work

2.3.5 Monitoring the validity and reliability of all analyses

2.3.6 Monitoring QA/QC requirements

2.3.7 Working with QA Officer to assure Quality Assurance and Control are not compromised

2.4 Quality Assurance (QA) Officer

The QA Officer is responsible for oversight and review of quality control data. As shown in the Organizational Chart, the QA Officer is free to make objective QA/QC assessments free from managerial influence. The QA Officer is not involved with day-to-day lab operations, but does have direct access to the Technical Director if any data quality dispute arises. In case of serious QA/QC issues, the QA Officer has the authority to suspend projects. Responsibilities include:

2.4.1 QC Programs, Accreditation, PE studies, data validation and integrity training

2.4.2 Creation and Distribution of SOPs and other QC documentation

2.4.3 General knowledge for data review

2.4.4 Arranging annual internal audits

2.4.5 Documenting policies and procedures for confidentiality and property rights

2.4.6 Documented training in QA/QC

2.4.7 Ensuring that all technical laboratory staff have demonstrated proficiency

2.4.8 Ensuring that the training of personnel is kept up-to-date

2.5 Technical Directors of Chemical Analysis

The Technical Directors of Chemical Analysis are responsible for the day to day operations in each analytical department. These departments are Inorganics, Organics, Conventionals, Metals, and Sample Prep. Additionally, they are responsible for ensuring that:

- 2.5.1 Data is double checked by a peer
- 2.5.2 Analyses are performed according to laboratory SOPs
- 2.5.3 Analysts adhere to Merit Labs chemical hygiene policies

2.6 Technical Staff

The technical staff who are responsible for analyses are expected to observe all QA/QC requirements that relate to their analyses. The staff has all training and experience pertaining to his or her expertise documented and kept with his or her training records, that include proficiency training, and on going demonstration of capability. In addition to technical training, Merit Lab's staff is obligated to follow the example for ethics written in the company code of ethics (Appendix F), which is also included in the training file.

2.7 Training

Training is a very important element of Merit Lab's Quality Assurance System (QAS) to ensure the competence of staff at all levels. Merit Lab's training program involves:

- 2.7.1 Demonstrations of the analytical procedure by the trainer to the trainee
- 2.7.2 Overseeing of the trainees initial attempts to perform analyses
- 2.7.3 Monitoring of the analytical results by the trainer until such time as the trainee has demonstrated competence
- 2.7.4 Updating training in case of changes in procedures
- 2.7.5 The primary expert for each particular procedure approves the training materials and procedures for trainee analysts. All Merit Labs technical and management staff participates in health and safety training. A copy of Merit Lab's chemical hygiene plan is on file. The sampling staff also has HAZWOP training (40 hours and eight-hour annual refresher course). All records are kept on file with individual personnel documentation.

2.8 Laboratory Capabilities

Merit Laboratories analyzes water, soil and air samples. A summary of Merit's services is in listed in Appendix G.

3.0 QUALITY ASSURANCE OBJECTIVES

The following are clarifications of Merit's quality objectives for measurement of data in terms of precision, accuracy, representativeness, comparability, and completeness. The specific application of these activities and tables associated with precision and accuracy data for each matrix can be found within their respective SOPs, MDL data, Instrument Demonstration of Capability, and training records.

3.1 Accuracy and Precision

- 3.1.1 Accuracy is the degree of agreement between an observed value and an accepted reference or true value.
- 3.1.2 Precision is a measure of the degree to which two or more measurements are in agreement.
- 3.1.3 These parameters are determined for every analyte of interest for each matrix. Quality control limits are established and evaluated in accordance with procedures described in each specific method. The main criteria in evaluating these limits are contained in each SOP. These limits are available in the methods for surrogate recoveries and recoveries of compounds of interest. These limits have to be evaluated annually on a matrix by matrix basis. It is important to mention that

for more accurate measurements of accuracy and precision, quality control samples must go through the same procedures associated with real samples. Quality control samples are spiked at a mid-level concentration for each matrix.

3.2 Completeness, Representativeness, and Comparability

- 3.2.1 Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions.
- 3.2.2 Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition within a defined spatial and/or temporal boundary.
- 3.2.3 Comparability is an expression of the confidence with which one data set can be compared to another.
- 3.2.4 These are not quantitative terms; rather they are a qualitative measure of the quality of the data. These three criteria are satisfied implicitly, providing that all of the quality control measures specific to a given method are followed and enforced.

3.3 Detection Limits

- 3.3.1 Method Detection Limits (MDL) are determined for all analytes as specified in the NELAC and EPA standards. MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte. MDL studies are performed on every method and matrix associated with that method for each analyte of interest. MDL studies are conducted on an annual basis. The MDL is performed and calculated using the equations and procedure defined in Merit's SOP# 060004 (Determination of Method Detection Limit). This SOP contains the most current equations, requirements, rules, and information pertaining to MDLs. The following minimum requirements must be met whenever possible.

- 3.3.1.1 It must be no less than 10% of the spiked value.

- 3.3.1.2 The average recovery must be between 60 and 140%.

- 3.3.2 For analytes for which spiking is a viable option, MDLs are determined by a MDL study. The MDL is initially determined for the compounds of interest in each laboratory method and for each matrix using pure reagent water, Ottawa sand, or other applicable matrix. The MDL study is executed by running "n" samples at up to five times the estimated method detection limit. Here, "n" is defined as the number of sample replicates, which must be seven or larger at the discretion of the analyst.
- 3.3.3 An MDL study is not performed for any component for which spiking solutions are not available. For these types of analytes, the MDL is based on the signal to noise ratio from the analysis of a QC check sample or calibration standard. When both signal to noise is not applicable and spiking solutions are not available the MDL is not applicable or must come from the method.
- 3.3.4 Quantitation Limit (QL), usually 3.18 times the MDL (as recommended by NELAC) is established. A Quantitation Limit is at or above the MDL and is supported the lowest non-zero standard in the calibration curve, adjusted by any sample preparation/extraction factors.
- 3.3.5 Reporting limits (RL) is the concentration listed on the Analytical Laboratory Report. The RL is greater than or equal to the QL. RLs fluctuate due to matrix, client request, and/or state/local requirements. RLs are subject to change and available to clients upon request. For OHIO VAP projects, only the RL term is utilized.

4.0 SAMPLING PROCEDURES

4.1 Records

- 4.1.1 Personnel with sampling duties are designated in the personnel files as Field Services.
- 4.1.2 All observations, data and calculations are recorded on field sheets.
- 4.1.3 A chain of custody must be filled out completely when Merits' field staff performs sampling.

4.2 General Requirements for Field Staff

- 4.2.1 Sampling personnel are employed by, or under contract to Merit.
- 4.2.2 All sampling personnel have sufficient education, training, technical knowledge, and experience.
- 4.2.3 Field personnel are responsible for any QA/QC requirements in the field.
- 4.2.4 Training for field personnel is documented in the training records.
- 4.2.5 All Merit sampling staff are HAZWOP certified and participate in the health and safety courses as well as the eight-hour refresher course for HAZWOP. In cases when Merits field personnel carry out sampling, the procedures used are documented as to the appropriateness to meet the client's needs. Appropriate statistical techniques for sample selection are recommended to the client.

4.3 Accommodation and Environmental Conditions

- 4.3.1 Samplers must ensure that field conditions do not invalidate results.
- 4.3.2 Any condition that might affect results is documented in the field log.

4.4 Sampling and Field Measurement Methods

- 4.4.1 Appropriate methods for sampling, transport, chain of custody, storage and preservation are strictly adhered to.
- 4.4.2 Sampling methods are performed to meet regulatory and client needs.
- 4.4.3 Non-standard methods are validated by Merit.

4.5 Equipment and Supplies

All field personnel are provided with the necessary sampling tools including automatic samplers, bailers, bottles, etc.

4.6 Documentation

All samples collected by Merit must include the following information on the Chain of Custody and in the field notes:

- 4.6.1 Client Report and Invoice Information, including address, phone numbers, and email address(if applicable)
- 4.6.2 Project name (i.e. Location of where the sample(s) were taken)
- 4.6.3 Name of sampler
- 4.6.4 Collected date and time of sample(s)

- 4.6.5 Sample tag(s) (i.e. Unique identifying name(s))
- 4.6.6 Sample Matrix
- 4.6.7 Number of containers and preservation
- 4.6.8 Analyses
- 4.6.9 Special Instruction(s) and/or Notes
- 4.6.10 Relinquished by and Received by Signatures

5.0 SAMPLE HANDLING

At Merit, samples are handled in accordance with EPA recommendations. Proper preservatives and holding times are used. Appendix I is a summary of preservation type and holding times based on the Code of Federal Regulations (CFR) and local state requirements. The samples are stored appropriately to maintain their integrity until the analyses are performed. This section summarizes policies and practices for sample handling. Further details are contained in specific SOPs.

Samples are accessible only to Merit staff in the building. Electronic locks secure the building. To increase security each set of doors has its own code, known only to Merit staff. These codes are changed whenever deemed appropriate.

5.1 Chain of Custody

- 5.1.1 Merit uses chain of custody records to document the possession of all samples from sampling to arrival at the lab. The chain of custody chronicles all of the time between sampling and log-in. All individuals who handled the sample are identified on the COC by signature. A copy of the chain of custody is left with each handler as a receipt. The COC is kept with the samples until log-in. All COCs are electronically scanned and stored in Merit's LIMs (Laboratory Information Management system). A copy of Merit's COC is in Appendix H.
- 5.1.2 All COC procedures are written in Merit Lab's SOP for Chain of Custody Preparation (SOP # 000025).

5.2 Sample Acceptance Policy

- 5.2.1 Merit has a written policy of the circumstances under which all samples must be accepted. This is part of the Sample Receiving SOP. Data from samples not satisfying the policy must be noted in the laboratory reports explaining the nature of variation. Merit policies require full documentation and labeling of each sample bottle including tag names, samplers, sample type, and preservation. Samples are checked at log-in for a number of parameters. These parameters are listed on Sample Receiving Checklist (Appendix L).

5.3 Sample Receipt Protocols

- 5.3.1 Upon receipt, the conditions of samples, including any abnormalities or departures from standard condition (as listed on the Sample Receiving Checklist) are recorded on the checklist. Samples are logged into VLIMS according to Merit's SOP for Sample Log-In.

5.4 Sample Tracking

- 5.4.1 Merit uses VLIMS, which uniquely identifies each sample for testing. A unique numeric identification is placed on each sample container. VLIMS includes a list of all analyses to be performed on each sample, including digestions and/or extractions.

- 5.4.2 Each action pertaining to a given sample set in VLIMS is saved in the "Sample Tracking Events" box in the Sample Manager of VLIMS. This box has been programmed so that it can not be edited by any user at any time. This box is clearly shown when a user looks up any sample in the Sample Manager and date and time stamped.

5.5 Storage Conditions

- 5.5.1 Samples are stored in separate walk-in coolers (one for solids and/or waste and the other for waters.) Water samples for metals do not require refrigeration and are stored in the Metals Prep Lab. Soil samples for metals are stored in solid/waste refrigerator. Volatile organic samples are stored separately from all other samples in a refrigerator in the Volatiles Prep Lab. Refrigerators are kept at specified temperatures and monitored daily. All standards are stored in separate refrigerators from samples, when required by method. Temperatures are monitored and recorded daily. See Refrigerator SOP (SOP #090001) for temperature requirements and corrective actions.

5.5 Sample Disposal

- 5.5.1 Merit holds all samples requiring refrigeration in refrigerators until the holding times for the samples expire, up to 30 days, unless requested otherwise by the client. At that time, the samples are moved to a storage area where they are disposed of, or sent back to the client. Samples are disposed of according to the SOP for Sample Disposal (SOP # 010003) and/or Sterilization of Regulated Samples (SOP #010011). All samples, digestates, leachates, extracts, or other preparation products are accumulated, stored, and disposed of in accordance with Federal and State laws. Merit maintains a Waste Disposal Manual with all necessary disposal documentation.

6.0 CALIBRATION PROCEDURES AND FREQUENCY

6.1 Traceability of Calibration

- 6.1.1 The overall program of calibration and/or verification and validation of equipment is designed and operated to ensure, whenever applicable, that measurements made by Merit are traceable to national standards of measurement when available. Calibration certificates must, whenever applicable, indicate the traceability to national standards of measurements and must provide the measurement results and associated uncertainty of measurement and/or a statement of compliance with an identified metrological specification.
- 6.1.2 When traceability to national standards of measurement is not applicable, Merit must provide satisfactory evidence of correlation of results, by participating in a suitable program for inter-laboratory comparisons or proficiency testing.

6.2 Reference Standards

- 6.2.1 Reference standards of measurement must be calibrated by a certified supplier that can provide traceability to the national standard of measurement. If the standards are not traceable, a regular check of in-house quality control using some type of secondary reference materials is performed.
- 6.2.2 All analytical balance calibrations are checked with Class S weights at the beginning of every day of use. All analytical balances are checked and calibrated for the range of use by a professional (NIST Certified) outside source annually. All documentation for all scales in the laboratory is kept on file. See Scale and Weight Calibration SOP (SOP # 060005) for specific requirements.

6.3 General Requirements

- 6.3.1 Merit documents the frequency, standards and calibration history of all analytical methodology and verifies and documents all working standards versus primary (reference) standards.

- 6.3.2 When relevant, all procedures for in-house calibration are documented. These include acceptance criteria and corrective action if equipment fails or falls outside these criteria. The specific staff member responsible for monitoring and for calibration implementation for each piece of equipment is identified and kept on file by the QA Officer.

6.4 Analytical Support Equipment

- 6.4.1 All ovens, refrigerators, and freezers are monitored for temperature. All oven thermometers are calibrated annually against NIST certified thermometers. All refrigerators are maintained at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and freezers are maintained at $0^{\circ}\text{C} \pm 4^{\circ}\text{C}$. Temperatures are monitored daily (working days only) and records of these temperatures are kept on file in a logbook. Thermometers in refrigerators and freezers are calibrated annually against NIST thermometers. Oven temperatures are monitored every day of operation.

6.5 Instrument Calibration

- 6.5.1 Calibration procedures for each specific laboratory instrument must consist of an initial calibration and a calibration verification, when an initial instrument calibration is not performed on the day of analysis. The SOP for each analysis performed in the laboratory describes the calibration procedures, their frequency, acceptance criteria and the conditions that require recalibration. In all cases, the initial calibration is verified using an independently prepared calibration verification solution. Merit maintains an instrument calibration logbook for each instrument which contains the following information: instrument identification, serial number, date of calibration, analyst, calibration solutions run, and the samples associated with these calibrations.
- 6.5.2 If the initial calibration fails, the analysis procedure is stopped and evaluated. For example, a second standard must be analyzed and evaluated or a new initial calibration curve must be established and verified. In all cases, the initial calibration must be acceptable before analyzing samples.
- 6.5.3 When an initial instrument calibration is not performed on the day of analysis, a calibration verification check standard is analyzed at the beginning of each batch. An exception to this policy is for internal standard methods (e.g. most organic methods). For these analyses, the calibration check is only analyzed at the beginning of the analytical sequence. The concentration of this calibration check varies as described in each method SOP.

6.6 Appropriate Grades of Reagents, Standards, and Gases

- 6.6.1 The standards and reagents used in Merit are certified to be the appropriate grade by the manufacturer consistent with its intended use. All reagents meet the recommendations in the analytical methods used at Merit.
- 6.6.2 All analysts keep track of their individual standards, stock solutions, and the reagents they use daily. The purity of the standards and reagents are marked on the labels and are referenced individually in the specific SOPs. Merit has two separate sources of standards and are for the most part NIST Traceable. Each analyst keeps track of the individual lot numbers and catalog numbers for the analyses. Please refer to the individual methods and SOPs for specific standards and reagents.
- 6.6.3 All working standards and stock solutions are used until the performance of the standards is not acceptable (i.e. falls outside the QC limits, etc.) or goes beyond the expiration date stamped by the manufacturer. Please refer to the individual SOPs for specific shelf life of standards and stock solutions.

- 6.6.4 All Merit's gases are purchased at the highest purity level available. The catalog and lot numbers are kept on file in the purchasing office. All gases with the exception of Argon go through a double purifying step (Supelco filter: Supelco carrier gas purifier) before entering the instruments.
- 6.6.5 All newly made standards and reagents are labeled including the initials of the analyst, date, unique identification number.
- 6.6.6 Traceability information is recorded in standard preparation logbooks. These logbooks vary slightly, but the following information must be recorded by all departments:
 - 6.6.6.1 Name of concentrated standard or reagent(s) used, lot number and manufacturer
 - 6.6.6.2 Date of preparation
 - 6.6.6.3 Date of expiration
 - 6.6.6.4 Unique Merit ID number

7.0 TEST METHODS AND STANDARD OPERATING PROCEDURES

Merit retains Standard Operating Procedures that describe all lab functions, from sample acceptance to sample disposal, including all test methods. All SOPs are available to all staff members. Originals are kept in the QA Officer's office and controlled copies are distributed to the appropriate analysts. Each SOP includes the effective date, the revision number, and the signature(s) of the QA Officer, Technical Director, and analysts to whom the SOPs are issued.

SOPs are used to ensure the method is followed consistently. All deviations from the listed procedures are documented during the analysis. Any deviations that can affect results are included on the analytical report, either as flags or as report notes.

7.1 SOPs for Administration

These SOPs describe Merit's administrative procedures. These procedures included but are not limited to the handling of documents and handling of sample data after analysis.

7.1.1. SOPs for Writing, Changing, and Distribution of SOPs

These SOPs detail the procedures for writing, changing and distribution of SOPs, to allow for optimization of processes while keeping analyses scientifically viable. These SOPs include the approval process through management.

7.2 SOPs for Sample Handling

These SOPs detail how samples and sample supplies (ie bottles and coolers) are handled that are not covered in test SOPs. These SOPs detail how Login and Disposal departments operate on a day to day basis.

7.3 SOPs for Field Services

These SOPs describe all essentials of laboratory field services and sampling.

7.4 SOPs for Sample Preparation

These SOPs cover topics, which might not always be included in the test methods and SOPs, that provide supplemental information such as analysis calculations, washing of glassware, and batch number tracking.

7.5 SOPs for Laboratory Test Methods

Procedures for test methods describing how the analyses are actually performed in the laboratory are specified in method SOPs. These SOPs cover sample preparation, cleanup, analysis, instrument calibration, data reduction, and QC requirements. They are based on reference methods published by the EPA, ASTM, AWWA, and other organizations as well as on internally developed methods validated according to the EPA's Performance-based Measurement System. Each method SOP includes:

- identification of the test method
- applicable matrix or matrices
- reporting limit
- scope and application, including components to be analyzed
- summary of the test method
- definitions
- interferences
- safety
- equipment and supplies
- reagents and standards
- sample collection, preservation, shipment and storage
- quality control
- calibration and standardization
- procedure
- data analysis and calculations
- method performance
- pollution prevention
- data assessment and acceptance criteria for quality control measures
- corrective actions for out-of-control data
- contingencies for handling out-of-control or unacceptable data
- waste management
- references
- any tables, diagrams, flowcharts and validation data.

See Appendix C for Analyses List of SOPs.

7.6 SOPs for Equipment Calibration and Maintenance

These SOPs detail the correct procedure for ensuring that laboratory equipment and instrumentation are in working order. Included in these SOPs are calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, and service arrangements for all equipment. Calibration and maintenance of laboratory equipment and instrumentation are done in accordance with manufacturers' specifications or applicable test specifications.

8.0 INTERNAL QUALITY CONTROL CHECKS

8.1 Laboratory Quality Control Samples

The data acquired from QC procedures is used to estimate the quality of analytical data, to determine the need for corrective action in response to identified deficiencies, and to interpret results after corrective action procedures are implemented. Each method SOP includes a QC section that addresses the standard QC requirements, acceptance limits, and corrective actions for the procedure. The internal QC checks might differ slightly for each individual procedure but in general are described below.

- 8.1.1 **Method Blanks** are performed at a frequency of one per batch of samples per matrix type per sample extraction or preparation test method. The results of these samples are used to determine batch acceptance.
- 8.1.2 **Laboratory Control Samples** (LCS, QC Check Samples) are analyzed at a minimum of one per batch of 20 samples per matrix type per sample extraction or preparation method except for analytes for which control standards are not available such as fractional organic carbon, total volatile solids, color, odor, temperature, or turbidity. The results of these samples are used to determine batch acceptance.
- 8.1.3 **Matrix Spikes (MS)** are analyzed at a minimum frequency of one in 20 samples per matrix type per sample extraction or preparation method except for analytes for which spiking solutions are not available or not appropriate (ie, total suspended solids). The sample(s) selected for spiking are rotated among received samples so that various matrix problems can be noted and/or addressed. Poor

performance in a matrix spike generally indicates a problem with the sample composition, and not the laboratory analysis, and is reported to assist in data assessment.

8.1.4 **Surrogates** - Surrogate compounds are added to all samples, standards, and blanks for all organic chromatography test methods except when the matrix precludes its use or when a surrogate is not available.

8.1.5 **Spike Components** - In general, all reportable components are in the spike mixes. However, in cases when the components interfere with accurate assessment (such as simultaneously spiking chlordane, toxaphene and PCBs in Method 608), the test method has an extremely long list of components (such as Methods 8270 or 6020) or components are incompatible, a minimum representative number (10%) of the listed components are used. The selected components of each spiking mix represent all chemistries, elution patterns and masses and include permit-specified analytes and other client requested components. All target analytes must be spiked at least once per year.

8.1.6 **Matrix Spike Duplicates (MSD) or Laboratory Duplicates** are analyzed at a minimum of one in 20 samples per matrix type per sample extraction or preparation test method. The selected sample(s) are rotated among received samples so that various matrix problems can be noted and/or addressed. Poor performance in the duplicates generally indicates a problem with the sample composition and is reported to assist in data assessment.

8.1.7 **Internal standard compounds** are added to all samples, standards, and blanks for GC/MS volatile and semi-volatile analyses as well as for ICP/MS metals analysis.

8.2 Selectivity

8.2.1 Absolute and relative retention times aid in the identification of components in chromatographic analyses and help evaluate the effectiveness of a column to separate constituents. Acceptance criteria for retention time windows are documented in each method SOP.

8.2.2 A confirmation is performed to verify a compound identification when positive results are detected on a sample from a location that has not been previously tested. Confirmations are performed on samples which have detectable hits, no history of detectable results from particular location, enough sample volume permits re-analysis, and client approval. Such confirmations are performed on organic tests except when the analysis involves the use of a mass spectrometer.

8.2.3 Acceptance criteria for mass spectral tuning are contained in SOPs.

8.3 Demonstration of Method Capability

8.3.1 Prior to acceptance and use of any method, satisfactory initial demonstration of method performance is required. This initial demonstration of method performance is performed each time there is a significant change in instrument type, personnel or test method. A Certification Statement is completed for each analyst documenting that this activity has been performed.

9.0 DATA REDUCTION, REVIEW, VALIDATION, REPORTING AND RECORDS

9.1 Data Reduction

Data from sample analysis is completely computerized in most cases. Computer programs used for data transfer are rigorously validated before use and verified through Level III validation. All information used in the calculations such as raw data, interference checks, and tuning records are recorded in order to enable reconstruction of the final result at a later date. Information on the preparation of the sample (e.g., weight or volume of sample used, percent dry weight for solids, extract volume, dilution factor used) is maintained in order to enable reconstruction of the final result at a later date.

9.2 Data Review

To detect transcription or calculation errors, a second analyst, supervisor, or QA Officer according to

laboratory procedures regularly reviews data. Spot checks are performed on computer calculations to verify program validity. Errors detected in the review process are referred to the analyst(s) for corrective action.

Note: OHIO VAP Special requirements

- All batches are reviewed.
- Organic and inorganic data review checklists are put in sample folders.
- Organic and inorganic data review checklists are included in Appendix J.
- Other OHIO VAP specific requirements are found in their respective SOPs.
- All records for the OHIO VAP are kept for minimum of ten years.
- Management or peer review must be performed on all manual integrations, see SOP #070001 (Peak Integration) for more information.

9.2.1 Data review is performed on the following key method parameters:

- Holding times and sample preservation
- Calibrations
- Blank analysis
- LCS analysis
- MS/MSD analysis
- Field duplicate analysis
- Surrogate recovery
- Internal standards performance
- Target analyte identification and quantitation
- Documentation completeness

The data review consists of three main steps. The analyst reviews all bench sheets, prep logs, results, and calculations for transcription and arithmetic errors. A peer reviews all bench sheets, prep logs, results, and calculations for transcription and arithmetic errors. Management (i.e. QA Officer and/or director of the department) reviews a minimum 20% of the reported data annually and 100% of QA/QC reported batch sample results. This review takes into account the following:

Chain of Custody Review:

Each shipment of samples to the laboratory has its own chain-of-custody record with client information, sample information, analyses, signatures, and other pertinent information written on the document. Verify that only one sample is written on each line of the chain of custody record and is not split among multiple lines. Verify that the chain of custody has a record of the possession transfer of samples, individuals relinquishing and receiving have signed, dated, and noted the time on the document. Verify that custody of samples between parties is continuous and time gaps do not occur. Verify the cooler temperature is noted on the chain of custody form. If the cooler temperature was greater than 6 °C at arrival, verify client notification. Verify that chain of custody has unique laboratory number written in the 'Merit Lab No.' section for each sample upon receipt.

Sample Set Receipt Review:

Verify that all information on Sample Set Receipt matches the information written on the chain of custody and is correct. The Sample Set Receipt with the Chain of Custody is sent to the client for review.

Quality Control Records Review:

Verify that all method and SOP required QC samples are analyzed and processed for each analytical batch. Verify that instrument tune contains all required analytes and are inside control limits according to applicable methods. Verify that calibrations meet instrument and applicable method requirements. Review method blank results for contaminants by analyte and verify that analytes on affected samples are flagged appropriately. Review laboratory control sample (LCS) results for low or high recoveries of applicable target compounds. Watch for the development of patterns or trends in LCS recoveries. Review matrix spike (MS) and matrix spike duplicate (MSD) samples for low and high recoveries of applicable compounds and flag analytes on affected samples appropriately. Verify that relative percent difference on matrix spike duplicate samples are within control limits. Review duplicate samples for relative percent difference (RPD) outside control limits. Review surrogate data

for applicable samples. If surrogates were outside control limits, verify that samples were re-analyzed if possible and if surrogates are still outside control limits that samples are flagged appropriately. Review internal standard data for applicable samples. If internal standards were outside control limits, verify that samples were re-analyzed if possible and if internal standards are still outside control limits that samples are flagged appropriately. Verify no values are reported less than MDL. Verify that the reporting limit is at or above the quantitation limit. Verify that data was flagged if reported less than quantitation limit.

9.3 Validation

Data validation is a process of determining the suitability of a measurement system for providing useful analytical data. This process involves the analytical data's quality assurance/quality control information is first compared to a series of QA/QC criteria. Based on the results of this comparison, the analytical data are then assigned qualifiers, which provide an indication of the data's usability. Typically, a third party validator performs an overall evaluation of the data's usability. Full validation is performed for each type of analysis on the collected samples. Full data validation, a Level III data deliverable, consists of a review of data summary forms and supportive raw analytical data.

Evaluation of laboratory data is performed utilizing the QA/QC criteria as listed in the method specific SOPs and the laboratory established control limits. Including:

- Field Duplicates
- Data Completeness
- Preservation & Technical Holding Times
- PT Samples/Accuracy Check
- Instrument Performance Checks
- Target Analyte Identification
- Initial & Continuing Calibrations
- Analyte Quantitation verification with Reported value
- Blanks Quantitation Limits
- Surrogate Compounds
- Internal Standards
- Matrix Spike/Matrix Spike Duplicate
- System Performance

Data qualifiers are assigned when the analytical data is validated, the analytical results and the associated QA/QC information are reviewed using the criteria specific to the analyses performed. Data qualifiers are commonly used during the third party data use to classify sample data as to its conformance to QC requirements. The most common conclusions are as follows:

1. Acceptable
2. Estimated (qualitatively correct, quantitatively suspect)
3. Rejected (data not suitable for any purpose)
4. Not Detected (specified detection limit)

The data qualifiers (1, 2, 4) gives the permission to report the data with notes to flag (2). The rejected data (3) requires re-analysis. The final interpretation of the flagged data corresponding to its appropriate qualifier is left for the data user.

Merit's internal procedures for data qualification are method specific and are dependent on the quality control outliers. The ranges for all quality control samples are specified in each method and the data is flagged accordingly.

9.4 Report Format and Contents

- 9.4.1 Merit summarizes the analytical results in a written report, which includes the Merit Lab Sample number, the client's description of the sample, and the analytical results. Laboratory analytical reports are signed by the Laboratory Director.

Note: OHIO VAP Special requirements

- Affidavits must accompany each analytical report.

- 9.4.2 The results of each test performed at Merit are reported accurately, clearly, unambiguously, and objectively in our analytical reports. Each report includes:

Analytical Report Coverpage

- Report ID
- Generated Date
- Client Information (Name, Address, Phone and/or Fax Number, Email Address)
- Name and address of Merit
- Report Summary
 - Lab Sample ID(s)
 - Project Name
 - Collected Date
 - Submitted Date and Time
 - Sampler Name
 - PO Number
 - Report Narrative (if applicable)
- Report Notes
- Approved Laboratory Signature with Job Title

Sample Summary Page

- Lab Sample ID(s)
- Client Sample Tag(s)
- Matrix
- Collected Date and Time

Sample Results Page

- Lab Sample ID
- Sample Tag
- Collected Date and Time
- Matrix
- COC Number
- Sample Containers
 - Number of Bottles
 - Type (Size and Material)
 - Preservative
 - Refrigeration
 - Arrival Temperature
 - Thermometer Number
- Results
 - Analysis
 - Results
 - Units
 - Reporting Limit (RL)
 - Method
 - Run Date and Time
 - Analyst
 - CAS Number
 - Flags (if applicable)
 - If an analytical report contains Flags, an explanation of the flag is included at the bottom of each page that the flag appears on.
 - MDL (if requested)

- 9.4.3 The bottom of every page in the analytical report contains the Client Name, Project Name, Page number and total number of pages, Report ID, and Generated Date.

- 9.4.4 Per client request results are flagged on a case by case basis as preliminary when the quality control samples are out of compliance. A new report is generated and distributed as soon as all quality control

samples are in compliance and reviewed. The analytical report must a note in the top right corner of the coverage stating if the report is preliminary, revised, or supplemental. If a revised or supplemental report is created in additional note is added to the coverage that the current report replaces the (01) report generated on the original date.

- 9.4.5 Other information relevant to a specific calibration or test, such as environmental conditions, measurements, examinations and derived results supported by tables, graphs, sketches, photographs, or any failures is included when appropriate.
- 9.4.6 Whenever the lab report includes expression of expert opinion as to the serviceability of the sample batch, suitability for specific purpose, or any other amplification of the test results, Merit notes that this amplification is not endorsed by accreditor. Merit clearly notes wherever analytical results are subcontracted. Merit's reports are individually standardized according to each client's needs.
- 9.4.7 Any amendments to the test report after its generation are made only in the form of a new document including the statement supplemental to the original report or a revised report. In the event that the analyst makes changes to the validated data, the sample automatically returns to the validation queue. The revised data cannot under any circumstances bypass the validation procedure. Only approved validation personnel have access to reporting files. Therefore, all software used for data manipulation undergoes validation.
- 9.4.8 Merit notifies clients promptly in writing if any event, such as the identification of defective equipment, casts doubt on the validity of results given in any test report or amendment to a test report. When specific circumstances (i.e. limited sample volume) cause deviation from written procedure, method, and/or SOP, this deviation must be accurately recorded and documented and appropriately processed and client must be informed of this fact with all information available.
- 9.4.9 Test results are certified to meet all requirements of the NELAC standards, or explanations are provided if they do not.
- 9.4.10 Out of hold time data requires special validation by the Project Managers. VLIMs software notifies Project Managers of analyses completed outside of specified hold times. The samples are sent to the special validation queue until released by Project Managers, QA Officer, or Technical Director. The special validation queue requires an explanation for why the analyses were completed outside of holding time. All outliers are flagged appropriately on the analytical report. Management is notified when sample is received within holding time but analyses were completed outside of holding time.

9.5 Records

- 9.5.1 Data documentation and record keeping are performed at Merit according to SOPs for recording and logging data. All data and other documents are recorded on special forms designed for a specific purpose, such as the chain of custody form or bench sheets. We maintain all laboratory data including hard copies from our laboratory instruments, chain of custody forms, and log books for a minimum of five years (10 years for Ohio VAP work).
- 9.5.2 Calculations and data transfers are subject to appropriate checks. The QA Officer determines the appropriate checks for the particular calculations and transfers.
- 9.5.3 Laboratory records generally consist of analysis bench books, personnel qualification and training forms, equipment maintenance logbooks, chain of custody forms, and sample receiving checklists. All records are recorded in indelible ink and retained for five years. Records that are stored or generated by computers have hard copy or write-protected backup copies.
- 9.5.4 Documentation errors are corrected by drawing a single line through the error so that it remains legible and is initialed by the responsible individual, along with the date of change. The correction is written adjacent to the error. If corrections need to be made in computerized data, a system parallel to the corrections for hand written data is used.

9.5.5 Laboratory records:

- 9.5.5.1 Standard Operating Procedures - Any revisions to laboratory procedures are written, dated, and distributed to all affected individuals to ensure implementation of changes.
- 9.5.5.2 Equipment Maintenance Documentation - All manuals are retained. The maintenance record of each system serves as an indication of the adequacy of maintenance schedules and inventory of spare parts. As appropriate, the maintenance guidelines of the equipment manufacturer are followed. When maintenance is necessary, it is documented in logbooks.
- 9.5.5.3 Calibration Records and Traceability of Standards/Reagents - The frequency, conditions, standards, and records reflecting the calibration history of a measurement system are recorded.
- 9.5.5.4 Sample Management - A record of all procedures to which a sample is subjected while in the possession of the laboratory is maintained. These include:
 - 9.5.5.4.1 The Sample Receiving Checklist (Appendix L). (See Section for 5.2.1 for details.)
 - 9.5.5.4.2 Disposal of hazardous samples including the date of sample or sub-sample disposal and name of the responsible person.
- 9.5.5.5 Original Data - The raw data and calculated results for all samples are maintained in laboratory notebooks, logs, bench sheets, files or other sample tracking or data entry forms. Instrumental output is stored in a computer file or a hard copy report. These records include:
 - 9.5.5.5.1 Laboratory sample ID code
 - 9.5.5.5.2 Date of analysis
 - 9.5.5.5.3 Instrumentation identification and instrument operating conditions/parameters
 - 9.5.5.5.4 Analysis type and sample preparation information, including sample aliquots processed, cleanup, and separation protocols
 - 9.5.5.5.5 All manual, automated, or statistical calculations
 - 9.5.5.5.6 Confirmatory analysis data, when required to be performed
 - 9.5.5.5.7 Analyst's or operator's initials/signature
- 9.5.5.6 QC Data - The raw data and calculated results for all QC samples and standards are maintained in the manner described in the preceding paragraph. This documentation allows correlation of sample results with the associated QC data. Documentation also includes the source and lot numbers of standards for traceability. QC samples include, but are not limited to, control samples, method blanks, matrix spikes, and matrix spike duplicates.
- 9.5.5.7 Correspondence - Correspondence pertinent to a project is kept and placed in the project files.
- 9.5.5.8 Deviations - All deviations from SOPs are reviewed and approved by the QA Officer or Technical Director.
- 9.5.5.9 Final Report - A copy of all reports generated and any supporting documentation is kept in VLIMS.
- 9.5.5.10 Administrative Records - The following are maintained:
 - 9.5.5.10.1 Personnel qualifications, experience and training records

9.5.5.10.2 Initial and continuing demonstration of proficiency for each analyst

9.5.5.10.3 A log of names, initials and signatures for all individuals who are responsible for signing or initialing any laboratory record

9.6 Document Control System

9.6.1 All operating procedures, manuals (including this Quality manual), and documents are subject to document control. Distribution of controlled documents is limited to those indicated on the document distribution list.

9.6.2 The purpose of the document control system is to ensure that only the most recent revisions are available to the appropriate personnel, revisions are timely, and receive the required approvals. All internal regulatory documentation, standard operating procedures, work instructions, service manuals, and product instructions are under document control. The QA Officer is responsible for the document control system and keeps a master list of the location of all documents and their current revision. The Technical Director and the QA Officer approve all newly revised documents. Any employee can request a change to a document. When necessary, obsolete documents must be retained for legal reasons or for knowledge preservation. The QA Officer stores retained obsolete documents. Each page of documents produced by the laboratory must contain the effective date, revision number, document number, and document title.

9.6.3 All quality documents (this Manual, SOPs, policies, etc.) are reviewed and approved by the QA Officer, the Technical Director, and/or the Laboratory Director. Such documents are revised whenever the activity described changes significantly. All documents are reviewed at least every two years.

9.6.4 All quality documents are controlled by the QA Officer. Controlled copies are provided to individuals in the laboratory who need copies. The QA Officer maintains a distribution list for controlled copies and ensures that any revisions are distributed appropriately.

9.6.5 In case Merit is for any reason dissolved, company records must be held for five years after the closing date. The owners of the company must retain the records at a known location (i.e., personal residence or storage facility).

9.6.6 Any sales agreement must contain a clause declaring that the new owners must maintain records for a minimum of five years. The records must also be available to clients during this time.

9.7 Confidentiality

9.7.1 All laboratory results and associated raw data are kept in confidence with the client who requested the analyses. Access to laboratory records and VLIMS data is limited to laboratory personnel except with the permission of the QA Officer or Laboratory Director and with permission of the client. NELAP-related records are made available to authorized accrediting authority personnel.

9.7.2 When clients require transmission of test results by telephone, email, facsimile or other electronic or electromagnetic means, staff must ensure confidentiality is preserved.

10.0 PERFORMANCE AND SYSTEM AUDITS AND FREQUENCY

10.1 Internal Laboratory Audits

10.1.1 Annual internal audits are performed to verify that laboratory operations continue to comply with the requirements of the quality system. The QA officer conducts such audits. The task of carrying out audits can be delegated to other staff with appropriate technical training and familiarity with the QAS. When the audit findings cast doubt on the validity of the laboratory's results, an immediate corrective action is initiated and any client whose work might be affected is notified.

- 10.1.2 The internal audit verifies that the operations continue to comply with the requirements of the laboratory's quality system. It is the responsibility of the QA officer to plan and organize the internal audits. These audits are most likely conducted during the lab's "slow" times, but at least once per year.
- 10.1.3 The internal audits include an examination of laboratory documentation on sample receiving, sample log-in, sample storage, COC procedures, sample preparation and analysis, instrument operation records, external calibration records, SOPs, and training records.
- 10.1.4 Quality assurance reports are provided to management summarizing the results, outliers, and corrective actions of the internal audits and yearly performance studies. The audit procedures must be documented. The audits are carried out in accordance with pre-planned program. The result of the audits are recorded.

10.2 Managerial Review

Merit Lab's internal management review includes the following objectives:

- 10.2.1 Management conducts an annual review of the quality system to ensure that the system is effective and still suitable. Also, if changes are needed, this review serves as a tool to implement improvements and changes to the quality system and overall laboratory operations. The review includes reports from management, the outcomes of recent internal audits, outcomes of external audits, PT results, any changes in the volume and type of work for the year, feedback from clients, corrective action reports and complaints. The lab maintains records of review findings and actions. This review functions to keep all staff informed on lab happenings on an annual basis. The managerial review must also include whether management objectives are being achieved and whether designated duties are being carried out satisfactorily.

10.3 Proficiency Test Study Participation

- 10.3.1 Merit participates in several Proficiency Test (PT) studies, see list below. Once the study results are released, the QA Officer reviews all of the analytes and any outliers are recorded. The out of control performances are documented and reviewed by both the analysts who performed the analyses, their direct management, and the QA Officer. A corrective action report documenting why the results were outside acceptable ranges is generated. These records are kept with the QA Officer and are included with the annual internal audit and management review.

Merit's Proficiency studies include:

- NELAP – semiannually
- WP– semiannually
- DMRQA– annually
- Drinking Water – annually

- 10.3.2 Review of Proficiency Test Studies documents any recurring trends or problems evident in PT studies and evaluates their effect on environmental data. All PT study results are tracked and compared with previous PT study results to find patterns or issues.

10.4 External Audits

- 10.4.1 Merit prepares and arranges audits by clients, accrediting bodies, regulatory agencies, and others to demonstrate the effectiveness of Merit's Quality Assurance System (QAS) and validity of the test results. If the audit cast doubt on the validity of certain results, then Merit must take immediate corrective action and immediately notify, in writing, any client whose work might have been affected.

The external system audits and the external proficiency test audits are performed biannually by an outside source (NELAP and MI Drinking Water), OHIO VAP Audits are conducted every 5 years. Some clients also perform their own external audits as needed (i.e. GM every 2 years, etc.).

The QA Officer is responsible for ensuring that all components of the laboratory's activities are audited on behalf of management. The task of carrying out audits can be delegated to other staff with appropriate technical training and familiarity with the QAS. The above described external audits are not a substitute for the lab's own internal audit. Merit must perform internal audits annually. Corrective action is undertaken within a reasonable time frame on all non-conformances identified within the QAS.

The QA Officer is responsible for maintaining records of all audits and ensuring that corrective action is undertaken. In exceptional circumstances, an external officer is appointed. The QA Officer is responsible for ensuring that the person appointed is familiar with the requirements of the QAS. Each aspect of the QAS must be audited at least once per year.

Documentation of Audit and Review Findings and Any Corrective Actions

The QA Officer ensures that documentation of the findings and corrective actions resulting from audits and reviews are discharged within the agreeable time scale. Corrective action is required whenever evidence arises that the system is not functioning properly.

1. Correction of an immediate failure might involve re-testing and/or withdrawing an invalid test report and issuing a new report.
2. Investigating the underlying cause of a failure might involve analysis personnel not being properly trained or the use of a new instrument.

11.0 FACILITIES, EQUIPMENT, REAGENTS, AND PREVENTATIVE MAINTENANCE

11.1 Facilities

- 11.1.1 Uninterrupted power supply (UPS): Our UPS system delivers constant power to all of our analytical instruments and computers, removing variations in power output such as surges, which can seriously damage electronic equipment. In addition, during a power outage, the UPS system keeps our instruments operating for two additional hours. This provides ample time to safely power down all instruments and to save analytical data that has been generated.

Our UPS has a built-in alarm system that notifies key Merit staff members any time that incoming power has been interrupted.

Since the UPS system has been operating, our downtime for instrumentation has been reduced by a factor of one half. Furthermore, despite some power interruptions due to weather, we have not seen any loss of data or lapse in turnaround time. Merit Labs invested in the UPS system so that we would be able to service our clients more reliably.

- 11.1.2 Gas Supply for Instrumentation: Merit's gas supply is located in a separate, ventilated area away from the main laboratory. The gas area includes Argon, Helium, Hydrogen, Nitrogen, and Oxygen. All gases have reserve tanks that are connected through automatic manifolds. This automatic system allows the instrumentation to be undisturbed and continuously working.
- 11.1.3 Air System: Merit has invested in a volume air system in order to:
- Increase the health and safety of our staff
 - Improve the quality of your data
 - Minimize cross contamination problems that all laboratories must deal with due to the nature of laboratory chemicals
- 11.1.4 The variable air system allows us to provide a safe testing environment:

- It delivers a constant supply of 100% fresh tempered air to every laboratory at a standard rate of six volume changes per hour.
- Each laboratory is self contained and sealed from other laboratories. If an accident occurs (i.e. spill of solvent, acid, etc.), then a responder to the spill must increase the fresh air flow in that specific laboratory to 30 air changes per hour. This emergency state is maintained until the spill is cleaned up and the situation is normalized.
- Particularly sensitive laboratories (the volatile analysis lab and extraction lab) are protected by air lock entry systems.
- Each laboratory has an independent pressure monitor and control system that maintains the required air pressure for each laboratory. For example, the extraction lab, which uses a number of volatile solvents, is maintained at a negative pressure. This helps to ensure that volatile solvents leave that lab exclusively through the fume hoods. On the other hand, our volatile laboratory is maintained at a positive pressure. This restricts the movement of volatile chemicals into this laboratory and prevents cross contamination.

11.1.5 Instant Capacity Increase

Merit's facility is designed to allow rapid addition of instrumentation and re-organization of the laboratory for more efficient utilization. All of the connections (electricity, gas, network, etc.) are externally mounted and are located conveniently throughout each laboratory. When we need to expand our instrumentation, we can quickly install it and start producing data almost instantly.

11.1.6 Security for your samples

Our building design prohibits access to any part of the facility by a visitor unless he or she is escorted by a Merit staff member. Samples can be conveniently delivered to us in our sample drop-off area inside the building without entering the laboratory portion of the facility. For your convenience, we provide secure after hours sample drop off lockers into our facility. These lockers are accessible to you 24 hours a day from outside our building. After samples are placed into a locker, it can be locked by the client in order to prevent it from being opened again from outside. The samples are then accessible only from inside the building.

11.1.7 Archive

Our archive system contains all the files in numerical lab ID order. All of the information is stored by project (i.e. analytical report, invoice, chain of custody record, raw data, etc.) These are stored in a specially organized archive for a period of time required by each specific project.

11.1.8 Emergency Response

Merit Laboratories, Inc. is responsive to our clients' needs in emergency situations. Therefore, we've streamlined our services and staff to address your emergency needs. If you run into problems anywhere in the country, we are available to help you find a solution. We have developed a reputation among our industrial clients for solving even the most difficult problems expediently, often over weekends and holidays.

11.2 Equipment and Reference Materials

11.2.1 The analytical lab is furnished with all items of equipment, including reference materials required for the correct performance of tests. When the lab needs to use equipment outside its permanent control, it ensures that the relevant requirements of this guide are met. List of all major equipment can be found in Appendix M.

11.2.2 Records are maintained for each major item of equipment and all reference materials significant to the tests performed. Records include:

11.2.2.1 The name of the item of equipment

11.2.2.2 The manufacturer's name, type, identification, and serial number or other unique identification

11.2.2.3 Current location, as appropriate

11.2.2.4 Details of maintenance carried out to date and planned for the future

11.2.2.5 History of any damage, malfunctions, modifications, or repair

11.2.3 Instruments that are broken are clearly tagged with Instrument Out of Order signs. Any instrumentation beyond repair is removed by laboratory area.

11.2.4 See Refrigerator SOP (SOP #090001) and Water Purity (DI) SOP (SOP #090002) for corrective actions and more information.

11.3 Documentation and Labeling of Standards and Reagents

11.3.1 The standards and reagents used by Merit are certified to be the appropriate grade by the manufacturer consistent with its use. All reagents meet the recommendations in the analytical methods used at Merit. Original containers sent by manufacturers are labeled with an expiration date.

11.3.2 All analysts keep track of their individual standards, stock solutions, and the reagents they use daily. The purity of the standards and reagents are marked on the labels and are referenced individually in specific SOPs. Merit has two separate NIST traceable sources of standards. Each analyst keeps track of the individual lot number and catalog number for the analyses. Please refer to the individual SOPs for specific standards and reagents.

11.3.3 The shelf life of calibration, stock, and working standards are specified by the manufacturer's expiration date. The expiration date is subject to acceptable use as defined by specific quality control parameters per individual SOPs. For more detail, please see Section 6.6 Appropriate Grades of Reagents, Standards, and Gases.

11.3.4 All newly made standards and reagents are labeled including the initials of the analyst, date, unique identifier, expiration date, and are traced back to its original components or reagents.

11.3.5 The quality of reagent water is monitored to meet method-specified requirements. Specifically, method blanks are performed in every department. Additionally, the laboratory uses an on-line conductivity meter to continuously monitor water quality.

11.4 Computers and Electronic Data Related Requirements

When computers or automated equipment are used for capturing, processing, manipulating, reporting, storing or retrieving of calibration or test data, Merit ensures that:

11.4.1 Compliance of all requirements of ISO IEC guide 25

11.4.2 Computer software is documented and adequate for use

11.4.3 Procedures are established and implemented for protecting the integrity of the data. Such procedures include, but are not limited to, integrity of data entry or capture, data storage, data transmission, and data processing

11.4.3.1 Merit's data storage and retrieval procedures are as follows: a hard copy of all data for a given sample is included in its respective file. This data includes, but is not limited to, a copy of a chain of custody, sample receiving checklists, any log in data and notes associated with the samples. The files with all hard copy data are stored on-site at Merit Labs. For analyses which are computerized, all raw data is stored electronically, either locally (on hard disk) for current data, remotely (on magnetic tape, diskette, or CD-ROM)

for older data. The physical location of electronic storage media is on site at Merit Labs. Non-computerized analyses have complete hard copy results stored Merit Labs in bench book format. When applicable, other hard copy data (i.e. recorder print-outs, etc.) are also stored. The hard copy of the data is kept for a minimum of 5 years on site.

- 11.4.4 Computer and automated equipment is maintained to ensure proper functioning and provided with the environmental and operating conditions necessary to maintain the integrity of the data, including the prevention of unauthorized access to and the unauthorized amendment of computer records

11.5 Preventative Maintenance

A routine preventative maintenance program is used to minimize the occurrence of instrument failure and other system malfunctions. Designated laboratory employees regularly perform routine scheduled maintenance and repair of all instruments. All maintenance that is performed is documented in the laboratory's appropriate maintenance logbook. Merit's Superintendent of Operations oversees all instrument maintenance, and Merit does not maintain service contracts. All laboratory instruments are maintained in accordance with manufacturer's specifications. To minimize instrument downtime the following steps are taken:

- 11.5.1 Periodic checking of the instrumentation
- 11.5.2 Supply of spare replaceable parts for immediate exchange are kept in the laboratory
- 11.5.3 Periodical preventative maintenance of some parts is performed (see attached Appendix K)
- 11.5.4 All of the documentation associated with a specific instrument is kept on file
- 11.5.5 All updates and revisions are tracked and documentation is retained
- 11.5.6 Collection of information for ordering better quality and more reliable parts is investigated and updated and catalogs are kept on file

11.6 Inspection/Acceptance Requirements for Supplies and Consumables

Labels indicating the following information on receipt and testing are to be used for critical supplies and consumables:

- 11.6.1 Unique identification number (if not clearly shown)
- 11.6.2 Date received
- 11.6.3 Date opened
- 11.6.4 Date tested (if performed)
- 11.6.5 Date to be re-tested (if applicable)
- 11.6.6 Expiration date

12.0 SPECIFIC ROUTINE PROCEDURES USED TO EVALUATE DATA QUALITY

- 12.0.1 Quality control acceptance criteria are used to determine the validity of the data based on the analysis of internal quality control check (QC) samples (see Section 8.0). The specific QC samples and acceptance criteria requirements are found in the laboratory SOPs. Typically, acceptance criteria are taken from published EPA methods. When no EPA criteria exist, laboratory generated acceptance criteria are established. Acceptance criteria for bias are based on the historical mean recovery plus or minus three standard deviation units, and acceptance criteria for precision range from zero (no difference between duplicate control samples) to the historical

mean relative percent difference plus three standard deviation units. Merit takes every corrective action to minimize qualification of data due to QC outliers.

- 12.0.2 Analytical data generated with QC samples that fall within prescribed acceptance criteria indicate the laboratory was in control. Data generated with QC samples that fall outside the established acceptance criteria indicate the laboratory was "out-of-control" for the failing tests. These data are considered suspect and the corresponding samples are reanalyzed or reported with qualifiers.
- 12.0.3 Many published EPA methods do not contain recommended acceptance criteria for QC sample results. In these situations, Merit uses 70 - 130% as interim acceptance criteria for recoveries of spiked analytes, until in-house limits are developed. In-house limits are based on a $\pm 3\sigma$ interval and must include a minimum of 15-20 data points (see, e.g., Method 8000B, section 8.7.3).

12.1 Laboratory Control Samples

A laboratory control sample (LCS) is analyzed with each batch of samples to verify that the accuracy of the analytical process is within the expected performance of the method. The results of the laboratory control sample are compared to acceptance criteria to determine usability of the data. Data generated with LCS samples that fall outside the established acceptance criteria are judged to be out of control. LCS data found to be out of control is reanalyzed if possible; otherwise a case narrative is provided explaining the deficiency.

12.2 Matrix Spikes/Matrix Spike Duplicates

Results from MS/MSD analyses are primarily designed to assess data quality in a given matrix, and not laboratory performance. In general, if the LCS results are within acceptance criteria, performance problems with MS/MSD results might either be related to the specific sample matrix or to an inappropriate choice of extraction, cleanup, or determinative methods. If any individual percent recovery in the matrix spike (or matrix spike duplicate) falls outside the designated acceptance criteria, Merit must determine if the poor recovery is related to a specific matrix effect or a laboratory performance problem. A matrix effect is indicated if the LCS data is within acceptance criteria but the matrix spike data exceed the acceptance criteria.

12.3 Surrogate Recoveries

Surrogates are exclusively used in organic analyses. Surrogate recovery data from individual samples are compared to surrogate recovery acceptance criteria in the methods. Surrogate outlier results are qualified when: reanalysis confirms the outlier, there is insufficient sample for reanalysis, or there is substantial non-target interference evident in the sample. For MS/MSD results, surrogate recoveries are used primarily to evaluate data quality of a single analytical run.

12.4 Internal Standard Recoveries

Internal standards are included in each analyzed sample for GC/MS volatiles, GC/MS semi-volatiles, and ICP/MS metals. For each analysis, the internal standard drift is monitored and compared with control limits. When the internal standard recovery falls outside of control limits, the appropriate compounds/analytes associated with that specific internal standard are flagged. Retention time windows must be verified. When there is evidence of matrix interference, samples need to be flagged in the analytical report. If there is evidence that the samples were prepared, analyzed or extracted incorrectly, then reanalyze the samples when possible, unless a matrix effect or high target compound concentrations are evident.

12.5 Method Blanks

- 12.5.1 Method blank analyses are used to assess acceptance of sample results. The source of contamination is investigated and measures are taken to correct, minimize the problem, or characterize (i.e. flag) results if the blank contamination exceeds the reporting limit. Samples corresponding to such a contaminated blank that potentially contain the detected analyte are reanalyzed if possible.
- 12.5.2 Each sample in the affected batch is assessed against the above criteria to determine if the sample

results are acceptable. Any sample associated with the contaminated blank is reprocessed for analysis or the results reported with appropriate data qualifying codes.

13.0 CORRECTIVE ACTION

13.1 Corrective action is the process of identifying, recommending, approving, and implementing measures to counter unacceptable procedures or out of control QC performance that can affect data quality. To the extent possible, samples are reported only if all quality control measures are acceptable. If a quality control measure is found to be out of control, and the data is to be reported, all samples associated with the failed quality control measure are reported with the appropriate flag(s). Sample results must also be qualified when holding times are not met, improper sample containers and/or preservatives are used, or when other deviations from laboratory standard practices and procedures occur.

The SOPs specify conditions that can automatically trigger corrective action or optional procedures. These conditions might include dilution of samples, additional sample extract cleanup, and automatic re-injection/reanalysis when certain QC criteria are not met.

13.2 When a complaint, or any other circumstance, raises doubt concerning the laboratory's compliance with the laboratory's policies or procedures, or with the quality of the laboratory's tests, the laboratory must ensure that those areas of activity and responsibility involved are promptly investigated. Records of the complaint and subsequent actions are maintained. Company procedure for dealing with complaints is referenced in the SOP for Complaints (SOP # 000002).

13.3 Corrective actions are performed for errors, deficiencies, deviations from laboratory procedures, laboratory events, quality control samples outside acceptance criteria that must be investigated based on unacceptable performance evaluation samples and client issues and/or complaints. The investigation of the problem and any subsequent corrective action taken is documented.

13.3.1 Documentation of corrective action includes the following

- Date
- Analysis
- Method and/or SOP if applicable
- Analyst
- Investigated by
- Problem(s)
- Description of event
- Resolution and/or Corrective action taken
- Completed by

13.4 Corrective Actions are followed up during internal audits and review of proficiency test studies. Internal Audits and PT studies can reveal issues that need corrective actions and/or information about the effectiveness of previous corrective actions.

13.5 The corrective action procedure is implemented for data outside control limits. Follow up on corrective action reports includes review of reanalysis, when available.

13.6 Any QC sample results outside of acceptance limits require corrective action. Once the problem has been identified and addressed, the corrective action can include reanalysis of samples, or results are appropriately flagged. Detailed corrective actions (i.e. quality control outlier, blank contamination, etc.) can be found in the SOPs.

13.7 Whenever testing discrepancies or departures from documented policies or procedures occur, the QA Officer is notified and Merit's SOP for validation and corrective action implemented. When specific circumstances (i.e. limited sample volume) cause deviation from written procedure, method, and/or SOP, this deviation must be accurately recorded and documented and appropriately processed and client must be informed of this fact with all information available.

14.0 SUBCONTRACTING AND SUPPORT SERVICES AND SUPPLIES

14.1 Subcontracting Laboratory Services

Clients are advised if any analyses are subcontracted to another laboratory. Any work that is subcontracted by Merit that is NELAP certified with Merit must be sent only to NELAP certified labs. The following records of all subcontracted analyses are maintained:

14.1.1 A copy of the subcontracted laboratory's scope of accreditation

14.1.2 A copy of the report from the subcontracted laboratory

14.2 Outside Support Services and Supplies

14.2.1 When Merit procures outside services and suppliers the lab must use only those outside support services and supplies that are of adequate quality to sustain the confidence in laboratory tests.

14.2.2 When no independent assurance of the quality of outside support services or supplies is available, the lab must have procedures to ensure that purchased equipment, materials, and services comply with specific requirements. Merit must, whenever possible, ensure that purchased equipment and consumable materials are not used until they have been inspected, calibrated or otherwise verified to comply with any requirements relevant to the method(s) of concern. The lab must maintain records of all suppliers from whom it obtained support services.

15.0 REFERENCES

1. ISO/IEC 25, General Requirements for Accreditation of Laboratories, April 1996
2. Quality Assurance Principles for Analytical Laboratories, fifth printing, 1988, Frederick M. Garfield, AOAC
3. Compilation of EPA's Sampling and Analysis Methods, W. Mueller & D. L. Smith, Lewis Publishers, Inc.1991
4. Guide to Environmental Analytical Methods, 2nd Printing, 1992, Genium Publishing Corporation
5. U.S. EPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 (most recent edition)
6. Standard Methods for the Examination of Water and Wastewater (most recent edition)
7. U.S. EPA Methods for Chemical Analysis of Water and Wastes (most recent edition)
8. Annual Book of ASTM Standards, Part 31, Water (most recent edition)
9. U.S. EPA Handbook for the Analysis of Solid and Hazardous Wastes (most recent edition)
10. NIOSH Manual of Analytical Methods (most recent edition)
11. Handbook of the Association of Analytical Chemists (most recent edition)
12. U.S. EPA Data Quality Objectives for Remedial Response Activities Development Process, EPA/540/G-87/003, March 1987
13. Quality Assurance of Chemical Measurements, John Keenan Taylor, Lewis Publishers, 1989
14. USEPA Handbook for Analytical Quality Control in Water and Wastewater Laboratories, Nation Environmental Research Center, Ohio, 1072
15. NELAC Quality Manual, National Laboratory Accreditation Conference, Catalyat Information Resources, L.L.C., 1999
16. Quality Manual, NELAC, 2003

APPENDIX A: CERTIFICATION STATEMENT

NELAC CERTIFICATION STATEMENT

The applicant understands and acknowledges that **Merit Laboratories, Inc.** is required to be continually in compliance with the National Environmental Laboratory Accreditation Conference (NELAC) standards and shall be subject to the penalty provisions provided therein.

I hereby certify that I am authorized to sign this application on behalf of the applicant/owner and that there are no misrepresentations in my answer to the questions on this application.

Merit Laboratories, Inc.

Signature
Laboratory Director

Name

Date

Signature
Quality Assurance Officer

Name

Date

Signature
Technical Director

Name

Date

APPENDIX B: INITIAL DEMONSTRATION OF CAPABILITY

A demonstration of capability (DOC) is made prior to using any test method, and at any time there is a significant change in instrument type, personnel or test method.

All demonstrations are documented through the use of the form in this appendix.

The following steps are performed.

- a) A quality control sample is obtained from an outside source. If not available, the QC sample is prepared by the laboratory using stock standards that are prepared independently from those used in instrument calibration.
- b) The analyte(s) are diluted in a volume of clean matrix sufficient to prepare four aliquots at the concentration specified, or if unspecified, to a concentration approximately 10 times the laboratory-calculated detection limit.
- c) At a minimum, four aliquots are prepared and analyzed according to the test method either concurrently or over a period of days.
- d) Using all of the results, the mean recovery and the standard deviation is calculated for each parameter of interest.
- e) The calculated mean and standard deviation are compared to the corresponding acceptance criteria for precision and accuracy in the test method (if applicable) or in laboratory-generated acceptance criteria (if there are not established mandatory criteria). If all parameters meet the acceptance criteria, the analysis of actual samples may begin. If any one of the parameters do not meet the acceptance criteria, the performance is unacceptable for that parameter.
- f) When one or more of the tested parameters fail at least one of the acceptance criteria, the laboratory repeats the test for all parameters that failed to meet criteria. If repeated failure occurs, the laboratory will locate and correct the source of the problem and repeat the test for all compounds of interest beginning with c).

CERTIFICATION STATEMENT

A copy of the certification statement is retained in the personnel records of each affected employee.

APPENDIX B

DEMONSTRATION OF CAPABILITY CERTIFICATION STATEMENT

Date: _____

Analyst: _____

Lab Department: _____

Matrix: ☐ Water ☐ Soil ☐ Oil/Waste

Methods: _____

SOP #s: _____

1. The analysts identified above, using the cited test method(s), which is in use at this facility for the analyses of samples under the National Environmental Laboratory Accreditation Program, have met the Demonstration of Capability.
2. The test method(s) was performed by the analyst(s) identified on this certification.
3. A copy of the test method(s) and the laboratory-specific SOPs are available for all personnel on-site.
4. The data associated with the demonstration capability are true, accurate, complete, and self-explanatory (1).
5. All raw data (including a copy of this certification form) necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well organized and available for review by appropriate assessors.

Signature
QA Officer

Date

Maya V. Murshak
Technical Director

Date

APPENDIX C: ANALYSES LIST OF SOPs

Supporting SOPs are available in the SOP Log

<u>Inorganic</u>	<u>Methodology</u>	<u>SOP Number</u>
Acidity	2310B (4a)	033101A
Alkalinities	2320B	033101B
Ammonia	4500-NH3 D	033503
BOD5/CBOD	10360	0310360
Carbon Dioxide	4500-CO2C	034500A
Chloride (titration)	325.3	033253
COD	410.4	034104
Conductivity	120.1	031201
Cyanide(colorimetric)	335.4/4500-CN E	033354
Cyanide Distillation	335.4/4500-CN E	03LACHATCN
Dissolved Oxygen	10360	0310360DO
Ferrous Iron	3500FeB/HACH8146	03HACHA
Hardness	2340	032340
Hexavalent Cr	3500Cr B/7196A	032184
Hexavalent Cr Digestion	3060A	033060
Ion Chromatography	300.0	033000
MBAS	5540C	034251
Nitrite	300.0	034500B
Phenols	420.1	034201
Phenols Distillation	LACHAT A	03LACHATA
Phosphorus	4500-P E	033652
Reactive Cyanide	9010B	039010
Residual/Total Chlorine	4500-Cl G	038167
Silica	4500Si D	034500
Sulfide Analysis	4500-S2 D	033762
Sulfide Distillation	LACHET B	03LACHETB
Sulfite	4500-SO3 2-B	030004
TKN	4500-N(org) / 4500-NH3 D	033514
TOC	5310C	034151
Turbidity	HACH T.2	03HACH
Density (liquid and powders)	2710F	032710B
Density (solid)	2710F	032710
pH (Liquid)	4500-H + B	031501
pH (Solid)	9045D	039045D
Total Dissolved Solids	2540C	031601
Total Solids/VS/Ash	2540B	031603
Total Suspended Solids/TVS	2540D	031602
Volatile Organic Content	EPA 25D/8260B/5035/D2369-81ASTM	030025D
Specific Gravity	ASTMD891A	03D891
Viscosity	ASTMD4212	034212
FOC by Walkley Black	Walkley Black	030002
Determination of H ₂ O ₂	KMnO ₄	030003

<u>Extractions</u>	<u>Methodology</u>	<u>SOP Number</u>
MBAS	425.1	044251
Oil & Grease (Freon, Grav.)	413.1	044131A
Oil & Grease (Freon, IR)	413.1	044131B
Oil & Grease (Hexane, Grav.)	1664A	041664A
Oily Waste Extraction	1330A	041330A
Oil & Grease Soxhlet		049071
PCB/Pesticides (soil)	3550B	043550
PCB/Pesticides (water)	3510C	043510
PCB Clean-Up	Misc.	043630C
PNA/BNA/TCLP/Herbs Ext.	3510C/3550B	043510C
BNA (soil)	3510C/3550B	043550B
TPH (Hexane, Grav.)	1664A	041664B
TPH (IR)	418.1	044181

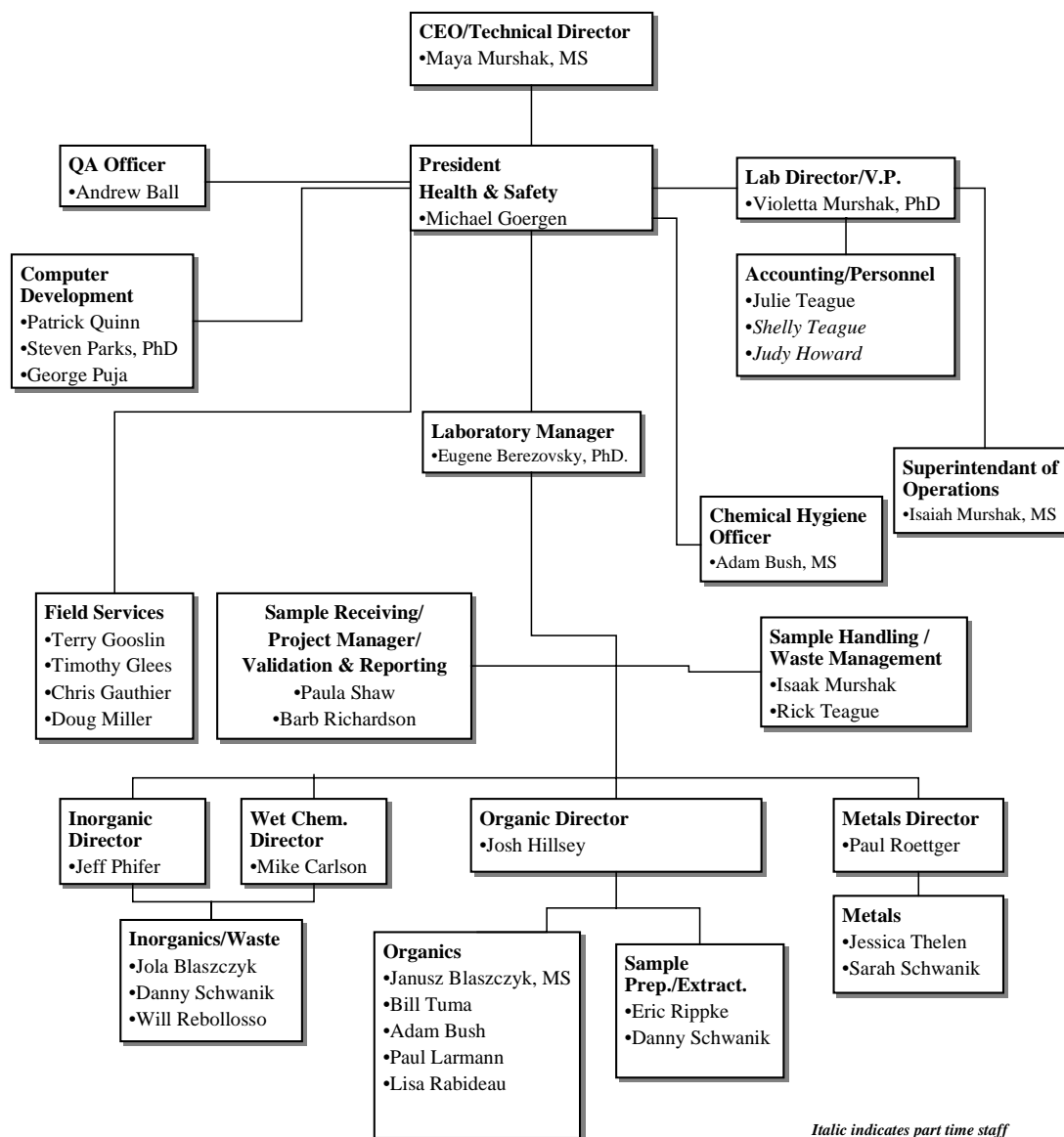
<u>TCLP/Waste Analyses</u>	<u>Methodology</u>	<u>SOP Number</u>
%Oil and % Water	ASTM D 96-88	059688
BTU/Total Halogens	D3286-85 Modified/5050	055050
Flash Point (Solid)	1030	051030
Flash Point (liquid)	ASTM D3278	05D3278
Paint Filter Test	9095	059095
SPLP Extraction	1312	050608
TCLP Extraction	1311	051311

<u>Organics</u>	<u>Methodology</u>	<u>SOP Number</u>
5035 Prep.	5035	075035
5035 Prep – VAP	5035	075035-VAP
Formaldehyde (HPLC & Ext.)	8315A	078315
PCBs by GC (Method 608)	608	070608
PCBs/	608/8082	078082
Pesticides	608/8081	078081
SVOCs/DRO	625/8270C/8015M	078270
VOCs/GRO	624/8260B/8015M	078260
VOCs/GRO – VAP	8260B/8015 B Modified	078260-VAP
Drinking Water VOCs	524.2	075242

<u>Metals</u>	<u>Methodology</u>	<u>SOP Number</u>
Digestion (Liquid)	3015A	083015
Digestion (Soil)	3050B	083050
Hg (Digestion & Analysis)	245.1/7470A/7471	087470
Hg Drinking Water	245.1	082451
ICPMS 200.8/6020	200.8/6020/6020A	082008

APPENDIX D: ORGANIZATIONAL CHART

Merit Laboratories, Inc. Organizational Chart



Rev. 09/09

Prepared by: Merit Laboratories, Inc.

Definitions of minimum level of experience and skill for positions in the laboratory:

The technical competence of the Merit Labs QAS program ensures that competent consulting chemists must be available to all clients to discuss the meaning of the analytical results or to address other technical areas of interest.

A. Management:

Merit Labs has the following management positions. They are:

1. CEO: Maya Murshak is responsible for the overall operation corporate goals and guiding the achievements of these goals. Responsible for all laboratory operations including technical development. Oversees all orders and resolutions of the Board and has general powers of supervision and management. Coordinates Merit Labs's sales marketing efforts. In her absence, the President, Mike Goergen, takes on her responsibilities.
2. President: Michael G. Goergen is responsible for executing corporate goals and guiding the achievements of these goals as set by the Board and CEO. Coordinates Merit Labs's training programs in health and safety. Provides clients with consulting and expert witness testimony. HAZWAP trained and certified. Expert in field sampling and environmental analyses, including biological testing. The CEO, Maya Murshak takes on Mike's responsibilities in his absence.
3. Vice President: Violetta Murshak, Ph.D. Vice Presidents, is in the absence or disability of the President perform the duties and exercise the powers of the President and performs duties as the Board of Directors or the CEO may prescribe. The Vice President(s) in combination with the President is (are) responsible for the general management of the laboratory. In Vice President's absence, the President and the CEO take over her duties.
4. Laboratory Director: Violetta V. Murshak, Ph.D. is responsible for all technical and financial areas of the company. The Laboratory Director is the signatory for all laboratory reports and invoices. Defines the minimum level of experience and skill necessary for all positions in the laboratory. Supervising all personnel and ensuring that outside support and services are of adequate quality to sustain confidence in the laboratory's tests. In her absence, the President and/or Technical Director take on her responsibilities.
5. Laboratory Manager: Eugene Berezovsky, Ph.D. is in charge of all technical areas of the laboratory and manages the sample through put and laboratory efficiency. Also in charge partially of instrumentation maintenance. The Laboratory Director takes place in his absence. In addition, the Superintendent of Operations takes place of instrument maintenance in his absence.

B. Technical:

All of MERIT LABS technical staff meets the minimum education and experience qualifications as posted by NELAC.

1. Technical Director: Maya V. Murshak, M.S., Merit's Technical Director is responsible for overall technical functions in the laboratory and Merit Labs' QAS and its implementation. All technical operations and support services are under the direction of Merit Labs Technical Director. The QAS is implemented and kept up to date by the QA Officer. Responsibilities include: certifying that staff is qualified for their positions, ensuring there is enough qualified staff to accomplish all work, monitoring the validity and reliability of all analyses and QA/QC requirements. Working with QA Officer to assure Quality Assurance and Control are not compromised. HAZWAP trained and certified. The Laboratory Director and/or the President cover for Maya in her absence.
2. QA Officer: Andrew Ball, Merit's QA Officer is responsible for all QC programs, including accreditation, PE Studies, creation and distribution of SOPs and other QC documents, reviews, internal audits, data validation, data review, and data integrity. In charge of document training and QA/QC manual training, as well as staff proficiency training and ensuring that the training of personnel is kept up-to-date. QCO answers directly to the Technical Director and CEO for all QAS functions. In the case of the QA Officer's absence, Technical Director takes on his responsibilities. Barb Richardson acts as support for QC reporting. Responsibilities include: Nominating deputies during absence, documenting policies and procedures for confidentiality and property rights.
3. Metal Analysts: Paul Roettger is the Metals director. His responsibilities include all metal analyses, statistical data, MDL studies, performance unknown samples, sample digestion and preparation, and instrument runs.

ICP/MS and Cold vapor analyzer. Jessica Thelen and Sarah Schwanik are analysts in the metals laboratory and are cross-trained to take place for one's absence.

4. Organic analysts: Josh Hillsey is the Organic director responsible for the entire organics department. Josh Hillsey for VOCs, Paul Larmann for SVOCs, Janusz Blaszczyk, MS for PCBs/Pesticides are responsible for the individual departments. They are cross trained on the different GC/MSs and GCs. All have extensive organic analyses background and are responsible for all organic data, QC samples, performance unknown samples, sample preparation (with the exception of extractables). Analysts include Bill Tuma, Lisa Rabideau, Adam Bush. In case of absence, the Organics Director can fill the position. In case of Organic Directors absence, the Technical Director is responsible.
5. Wet Chemistry/Inorganics Analysts: Jeff Phifer and Mike Carlson are both cross-trained on all conventional analyses. Both Mike and Jeff have extensive experience and background in all wet chemistry analyses. They are responsible for running all conventional analyses and instrumentation (ion chromatography, Hach, Discrete analyzer). Jola Blaszczyk is an analyst in the wet chemistry department and has been trained in all titration analyses, ferrous iron, FOC, chlorine, hexavalent chromium, phenols and titration chlorides. BOD, DO and pH analyses are completed by Danny Schwanik and Will Reboloso. In case of their absence, Barb Richardson is responsible for the analyses.
6. Extraction and conventional Analysts: Danny Schwanik and Eric Rippke, are cross-trained for all sample preparations for all matrices (i.e. sample extractions). They are also responsible for all IR methods (i.e. 418.1 for TPH IR, Oil and Grease, etc.). Paul Larmann and Adam Bush are support staff for extractions.
7. Waste Characterization/TCLP: Will Reboloso and Danny Schwanik are responsible for waste characterization and TCLP extraction preparations. They are cross-trained to cover each other. Barb Richardson acts as a support and back-up in case of both are absent.
8. Superintendent of Operations: Isaiah Murshak, MS is responsible for all instrumentation maintenance, record keeping, spare parts ordering, and repairs. Isaiah has extensive education, experience, and individual training in instrumentation maintenance. Eugene Berezovsky (Laboratory Manager) is cross trained to cover maintenance issues.
9. Sample Log-in/Report Validation/Invoicing/Lab Project Management: Paula Shaw and Barb Richardson are responsible for all sample log-in, reporting, invoicing, and final report validation, as well as client services and relations. They are cross-trained to cover each other in case of absence. In case of both parties being absent, Pat Quinn and Maya Murshak are trained in this area. In case of everyone being absent, the QA Officer covers their positions.
10. Client Relations/Field Sampling: Tim Glees, Chris Gauthier and Doug Miller are responsible for all sampling, sample pick-up, and client relations. Chris Gauthier and Tim Glees are responsible for bottle orders and is cross-trained with Mike Goergen, Maya Murshak, and Andy Ball on field sampling and sample pick-up.
11. Computer/Software Development: Patrick Quinn, George Puja, and Steven Parks, Ph.D. are responsible for all network systems, data backup and archive procedures, as well as automating reports, electronic deliverables, and computerized quality control data. George Puja is responsible for on-line reporting. Steve Parks, Ph.D. acts as support staff in case of absence.
12. Accounting/Personnel Director: Julie Teague is responsible for all-financial bookkeeping, audits, and payroll. Julie is cross-trained with the vice president in case of her absence. Julie also keeps all personnel records that show training and conference attendance. Julie also tracks all supplies that are ordered. In case of Julie's absence, Violetta Murshak is responsible for her duties.
13. Sample Handling/Waste Management: Rick Teague is the sample coordinator that handles the sample disposal efforts. Isaak Murshak is responsible for Merit's Waste Disposal and Hazardous Waste Management Manual. Isaak Murshak coordinates disposal of hazardous. Mike Goergen covers for Isaak Murshak in case of absence.
14. Chemical Hygiene/Health & Safety: Adam Bush is responsible for all chemical hygiene and health and safety training. Mike Goergen is responsible for setting up all Chemical Hygiene and Health and Safety Programs and takes Adam's place in his absence.

APPENDIX E: GLOSSARY

Accreditation Criteria: A set of requirements used by an accreditation system that a laboratory must meet in order to be accredited.

Accuracy: The closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy must be a combination of a random component and of a common systematic error (or bias) component. The nearness of a result or the mean of a set of results to the true or accepted value. Accuracy can be assessed by comparing the true values with mean of a set of experimental results. These results are done on different matrices that are spiked at a mid point concentration values that undergo the same sample preparation procedure and measurement as the samples and an average recovery value is obtained. Accuracy can be expressed in the following equation: Where: T = True value R = Measured value (mean of multiple measurements)

Batch: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less must all be handled as a separate batch.

Bias: A systematic displacement of all the observations in a sample from the true or accepted value, or a systematic and consistent error in test results.

Blank: An artificial sample designed to monitor the introduction of artifacts in the process. For aqueous samples, reagent water is used as a blank matrix; however a universal blank matrix does not exist for solid samples. The blank is taken through all the appropriate steps of the sample preparation and analysis process.₂

Blank Spike: A laboratory-prepared check standard prepared in deionized water.

Calibration: The set of operations which establish, under specified conditions, the relationship between values indicated by a measuring instrument or measuring system, or values represented by a material measure, and the corresponding known values of a measurement.₁

- a. Calibration - (Inorganic Analysis) The establishment an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type of acid and reagents or concentration of acid as used in the sample preparation.
- b. Calibration Blank - (Inorganic Analysis) Usually an organic or aqueous solution that is as free of analyte as possible and prepared with the same volume of chemical reagents used in the preparation of the calibration standards and diluted to appropriate volume with the same solvent (water or organic) used in the preparation of calibration standards. The calibration blank is used to give the null reading the instrument response versus concentration calibration curve. One calibration blank must be analyzed with each analytical batch or every method-specified number of samples, whichever is greater.
- c. Calibration Check - Verification of the ratio of instrument response to analyte amount, a calibration check is done by analyzing for analyte standards in an appropriate solvent. Calibration check solutions are made from a stock solution that is different from the stock used to prepare standards.
- d. Calibration Check Standard - Standard used to determine the state of calibration of an instrument between periodic recalibration.
- e. Calibration Standard - A series of known standard solutions used by the analyst for calibration of the instrument (i.e. preparation of the analytical curve).

Calibration Method: Defined technical procedure for performing a calibration.

- a. Initial Calibration - Analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the analytical detector or method.
- b. Instrument Calibration - Analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.
- c. Instrument Check Standard - A multi-element standard of known concentration prepared by the analyst to monitor and verify instrument performance on a daily basis.

Certified Reference Material (CRM): A reference material whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body.

Control Sample: A QC sample introduced into a process to monitor the performance of the system.

Field Blank: Sample of analyte-free media similar to the sample matrix that are transferred from one vessel to another or exposed to the sampling environment at the sampling site. They are used to measure incidental or accidental contamination of a sample during the whole process (sampling, transport, sample preparation, and analysis). Capped and cleaned containers are taken to the sample collection site. Usually at least one field blank with a matrix comparable to the sample of interest is collected with each batch of samples.

Good Laboratory Practices: A set of rules, operating procedures, and practices as established by a regulatory agency that are adequate to ensure the quality and integrity of data generated by a laboratory.

Instrument Blanks: Solvent or reagent blanks used to measure interference or contamination from an analytical instrument by cycling matrices containing materials that are normal to the analysis (but minus the analytes of interest through the instrument).

Intra-laboratory quality control: A continuing, systematic, in-house regimen intended to ensure the production of analytical data of continuing high quality.

Laboratory blank: See method blank

Laboratory Control Sample: A known matrix spiked with compound(s) representative of the target analytes. This is used to document laboratory performance.

Limit of quantitation: The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The limit of quantitation is generally 5 to 10 times the MDL. For many analytes the limit of quantitation analyte concentration is selected as the lowest non-zero standard in the calibration curve. Sample limits of quantitation are highly matrix dependent. (As seen in SW-846 Chapter 1 under estimated quantitation limit as of June 16, 2010).

Matrix: The component or substrate (e.g., surface water or drinking water) which contains the analyte of interest.

Matrix Duplicate: An intra-laboratory split sample which is used to document the precision of a method in a given sample matrix.

Matrix Spike: An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

Matrix Spike Duplicates: Intra-laboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank must be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank of any analyte of concern must not be higher than the highest of either:

- (1) The method detection limit, or
- (2) Five percent of the regulatory limit for that analyte, or
- (3) Five percent of the measured concentration in the sample.

Method Detection Limit (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix type containing the analyte. Additional information is available in the MDL SOP, SOP#060004.

Precision: The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. These samples must contain concentrations of analyte above the MDL, and can involve the use of matrix spikes. The most commonly used parameter for estimation of precision is the relative standard deviation (RSD) or the coefficient of variation (CV),

$$RSD = CV = 100 \frac{S}{\bar{x}}$$

where: \bar{x} = the arithmetic mean of the x_i measurements
 s = variance; and the relative percent difference (RPD) when only two samples are available.
RPD is defined as follows:

$$RPD = 100 \frac{|x_1 - x_2|}{\left[\frac{x_1 + x_2}{2} \right]}$$

Preventative Maintenance: An orderly program of positive actions for preventing failure of equipment and ensuring, in so far as possible, that the equipment is operating with the reliability required for quality results.

Primary Reference Standard: A homogeneous material with specific properties, such as identity, purity, and potency that has been measured and certified by a qualified and recognized organization.

Proficiency Testing: A process whereby a laboratory tests samples from an outside source. The concentrations of the samples are known to the supplier, but are unknown to the laboratory. The laboratory reports its results to the supplier, who then evaluates those results. Also known as performance evaluation studies or blind studies.

QAS: Quality Assurance System

QASO: Quality Assurance System Officer

Quality Control: A planned system of activities whose purpose is to provide a quality product.

Quality Manual: A document stating the quality policy, quality system and quality practices of an organization.

Quality Assurance: A planned system of activities whose purpose is to provide assurance that the quality control program is actually effective.

Quality System: The organization structure, responsibilities, procedures, processes and resources for implementing quality management.

Quantitation Limit: See Limit of Quantitation

Range: The difference between the maximum and minimum values of a set of values.

Reference Material: A material or substance in which one or more properties are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

Reference Standard: A standard, generally of the highest metrological quality available at a given location, from which measurements made at that location are derived.

Relative Standard Deviation (RSD): A measure of precision that is calculated as the standard deviation of a set of values divided by the average and usually multiplied by 100 to be expressed as a percentage.

Reliability: The ability of an item or a system to perform a required function under stated conditions for a stated period of time.

Repeatability: The precision, usually expressed as a standard deviation, that measures the variability among results of measurements at different times on the same sample at the laboratory.

Replicates: Repeated, but independent, determinations on the same sample by the same analyst at essentially the same time and under the same conditions.

Reporting Limit: The RL is the reporting limit used for analytical results. The value must be higher than or equal to the MDL. If the reporting limit is below the quantitation limit then the data must be flagged accordingly. RLs are stored in the LIMS and can be provided to any clients and/or auditors upon request.

Representative Sample: A subset or group of objects or things selected from a larger set designated as a "lot" or "population."

Reproducibility: The precision, usually expressed as a standard deviation, which measured the variability among results of measurements of the same sample at different laboratories.

Surrogate: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples.

System Audit: An on-site inspection or assessment of a laboratory's quality control system.

Test: A technical operation that consists of the determination of one or more characteristics or performance of a given product, material, equipment, organism, physical phenomenon, processor service according to a specified procedure.

Test Method: Defined technical procedure for performing a test.₁

Traceability: The property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons.₁

Trip Blank: A sample of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. A trip blank is used to document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organics samples.

Verification: Confirmation by examination and provision of evidence that specified requirements have been met.₁

APPENDIX F: CODE OF ETHICS

Merit Laboratories is committed to ensuring the integrity of its data and meeting the quality needs of its clients. We pledge to manage our business according to the following principles:

- To produce results that are technically sound and legally defensible
- To assert competency only for work for which adequate equipment and personnel are available
- To present services in a confidential, honest, and forthright manner
- To have a clear understanding with the client as to the extent and kind of services to be rendered
- To provide employees with guidelines and an understanding of the ethical and quality standards required in this industry
- To operate facilities in a manner that protects the environment and the health and safety of employees and the public
- To obey all pertinent federal, state, and local laws and regulations; under penalty of jail and/or fines
- To continually improve product and service quality
- To treat employees equitably, acknowledge their scientific contributions, and provide them with opportunities for professional growth and development
- To deal openly, honestly, and fairly in all business and financial matters with employees, clients and the public
- To ensure proper documentation is kept on all business activities and records are unambiguous, accurate, and up-to-date.
- To notify clients of any changes that might affect data.
- To ensure sample integrity for all samples to the best of the laboratory's ability.

APPENDIX G: SCOPE OF SERVICES

VOLATILE ORGANICS

Appendix IX Volatiles
TCL Volatile Organic Compounds
Aromatics, BTEX (624/8260)
Total Petroleum Hydrocarbons (GRO-GC, CA 8015M)
GC/MS for Volatile Organics (624/8260)
Drinking Water Volatiles (524.2)

SEMI-VOLATILE ORGANICS

Appendix IX Semi-Volatile Organics
TCL Volatile Organic Compounds
Phthalate Esters (625/8270)
PCB (608/8082) & clean-up procedures (ex. Sulfur, Acid, Alumina)
Organochlorine Pesticides (8081)
GC/MS for Semivolatile Organic, BNA (8270)
Chlorinated Hydrocarbons/PCB/Pesticides (603/8081/8082)
Total Petroleum Hydrocarbons (DRO, CA 8015M)

WASTE ANALYSIS

Total TCLP parameter content (no extraction)
Total TCLP Analyses
Total TCLP w/o Herbs & Pests
TCLP Semivolatile Organics (GC/MS)
TCLP Herbicides & Pesticides
TCLP Volatile Organics
TCLP Metals (8 RCRA Metals)
TCLP Metals (MI 10 RCRA Metals)
Corrosivity, pH
Ignitability, Flash Point
Paint Filter Test
Reactivity (Cyanide, Sulfide)
Density
General Observations
Total Solids
Total Ash Solids
Total Volatile Solids

ELECTRONIC FORMATS

MS Excel
Adobe PDF
EQUIS Formats
TERRA based formats
Customized Electronic deliverables
MDEQ EDDs
Electronic CLP-like format Level III deliverables

DATA ACCESSIBILITY

Online reference at www.meritlabs.com:

- ♦ Laboratory personnel contact information
- ♦ Approved methodologies reference
- ♦ Sampling reference data (analysis-appropriate list of containers and preservatives)

Soon available to all of our clients:

- ♦ Electronic acquisition of your data online
- ♦ Online data management tools
- ♦ Secure access only by authorized data users

Contact us at (517) 332-0167, for more information.

METALS ANALYSIS

Individual Metals via ICP/MS (6020/200.8):

<i>Aluminum (Al)</i>	<i>Cobalt (Co)</i>	<i>Selenium (Se)</i>
<i>Antimony (Sb)</i>	<i>Copper (Cu)</i>	<i>Silver (Ag)</i>
<i>Arsenic (As)</i>	<i>Iron (Fe)</i>	<i>Sodium (Na)</i>
<i>Barium (Ba)</i>	<i>Lead (Pb)</i>	<i>Thallium (Tl)</i>
<i>Beryllium (Be)</i>	<i>Magnesium (Mg)</i>	<i>Tin (Sn)</i>
<i>Boron (B)</i>	<i>Manganese (Mn)</i>	<i>Titanium (Ti)</i>
<i>Cadmium (Cd)</i>	<i>Nickel (Ni)</i>	<i>Vanadium (V)</i>
<i>Chromium (Cr)</i>	<i>Potassium (K)</i>	<i>Zinc (Zn)</i>
<i>Calcium (Ca)</i>	<i>Others upon request</i>	

Mercury (Hg) (0.2 ppb) (245.1/7471A)

RCRA Metals/MI 10 Metals/PPO Metals (13)/TAL Metals

Semiquantitative Scan-60 metals ICP/MS only

CONVENTIONAL ANALYSES

Acidity (2310B (4a))	Hardness (CaCO ₃) (2340)
Alkalinity (CaCO ₃) (2320B)	MBAS (5540C)
Ammonia (NH ₃) (4500-NH3D)	Nitrate (NO ₃ -N) (300.0)
BOD/CBOD/DO (10360)	Nitrite (NO ₂ -N) (300.0)
BTU (D3286-85 M)	Total Kjeldahl Nitrogen (TKN)
Chloride (Cl ⁻) (300.0)	(4500-N(org)/NH ₃)
Chlorine (Cl ₂) (4500-Cl G)	Oil/Grease (Hexane 1664A)
COD (410.4)	TPH-IR (418.1)
Conductivity (120.1)	Phenols (420.1)
Chromium, Hexavalent (Cr VI)	Phosphorus, Ortho (4500-P E)
(3500-Cr B/7196A)	Phosphorus, Total (4500-P E)
Cyanide, Amenable (CN ⁻)	Solids, Dissolved (2540C)
(335.4/4500CN G)	Solids, Suspended (2540 D)
Cyanide, Total (CN ⁻)	Sulfate (SO ₄) (300.0)
(335.4/4500CN E)	Sulfide (S ²⁻) Total/Dissolved
Density (2710F)	(4500-S2D)
Fluoride (F ⁻) (300.0)	
Halogens (5050)	

SCOPE OF SERVICES

- ♦ Electronic deliverables of your data in any format that you request including EQUIS, Excel, Envirodata, MDEQ, etc.
- ♦ Capacity to handle large volumes of work, especially in EMERGENCIES.
- ♦ Our analysts have a minimum Bachelors in the fields of chemistry, physics, or chemical engineering. 30% of our staff have Masters and Ph.D. degrees.
- ♦ We are centrally located and can conveniently service many states including the mid-west, east coast and southern states.
- ♦ We are located in a state of the art 18,000 ft² environmental laboratory facility that allows us to meet the highest existing QA/QC requirements including CLP-like deliverables and raw data packages both in electronic and hard copies.
- ♦ Merit holds several accreditations, including OHIO VAP certification, Michigan, New York, Florida and Indiana.
- ♦ We provide the flexibility to service any of your needs which might include: additional state accreditations, supplemental QC requirements, customized data deliverables, and increasing capacity quickly.

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Prepared by: Merit Laboratories, Inc.

APPENDIX I: HOLDING TIME TABLE REFERENCES

ANALYSIS	BOTTLE TYPE	HOLD TIME ¹	METHOD	MATRIX
Acidity	250 mL Plastic None	14 days	2310B (4a)	Liquid
Alkalinity	250 mL Plastic None	14 days	2320B	Liquid
Ammonia	250 ml Plastic H ₂ SO ₄	28 days	4500-NH3 D	Liquid
	4 oz Glass Jar None			Solid
BOD/CBOD	1 L Plastic None	2 days to set-up, 5 days to read	10360	Liquid
BTU	4 oz Glass Jar None	365 days	D3286-85 Mod	Liquid/Solid
Carbon Dioxide	500 mL Plastic None	24 hours	4500-CO2C	Liquid
Chloride	250 mL Plastic None	28 days	300.0	Liquid
	4 oz Glass Jar None			Solid
Chlorine (Total/Residual)	250 mL Plastic None	ASAP	4500-Cl-G	Liquid
COD	250 mL Plastic H ₂ SO ₄	28 days	410.4	Liquid
Conductivity	250 mL Plastic None	14 days	120.1	Liquid
Cyanide (Total/Amenable)	125 mL Plastic NaOH	14 days	335.4/335.2/ 4500-CN-E	Liquid
	4 oz Glass Jar None			Solid
Cyanide (Available)	1 250 mL Amber NaOH 1 250 mL Amber PbCO ₃ 1 250 mL Amber NaOH/PbCO ₃	14 days	OIA-1677	Liquid
Cyanide (Reactive)	4 oz Glass Jar None	14 days	9010B	Liquid/Solid
Density	125 mL Plastic None	14 days	2710F	Liquid/Solid
Dissolved Oxygen (DO)	500 mL Plastic None	24 hours	10360	Liquid
Ferrous Iron	2 40 ml VOA HCl	14 days	3500FeB/ HACH8146	Liquid
Flash Point	125 mL Plastic None	14 days	ASTMD3278	Liquid
	8 oz Glass Jar None	365 days	1030	Solid
Fractional Organic Carbon (FOC)	4 oz Glass Jar None	28 days	Walkley Black	Solid
Fluoride	250 mL Plastic None	28 days	300.0	Liquid
Halogens	4 oz Glass Jar None	28 days	5050	Liquid/Solid
Hardness	125 mL Plastic HNO ₃	180 days	2340	Liquid
Hexavalent Chromium (Cr VI)	125 mL Plastic None	24 hours	3500-Cr B/ 7196A	Liquid
	4 oz Glass Jar None	30 days ²		Solid
MBAS	500 mL Plastic None	48 hours	5540C	Liquid
Metals	125 mL Plastic HNO ₃	180 days	6020/6020A/ 200.8	Liquid
	4 oz Glass Jar None			Solid
Mercury	125 mL Plastic HNO ₃	28 days	7471A/245.1	Liquid
	4 oz Glass Jar None			Solid
Mercury (Low Level ng/L)	2 40 mL VOA None	28 days	1631E	Liquid
Nitrate (NO ₃ -N)	250 mL Plastic None	48 hours	300.0	Liquid
Nitrite (NO ₂ -N)	250 mL Plastic None	48 hours	300.0	Liquid
Nitrate & Nitrite	250 mL Plastic None	28 days	300.0	Liquid
ANALYSIS	BOTTLE TYPE	HOLD TIME ³	METHOD	MATRIX

¹ Holding time starts from the end of sample collection and ends when analyzed unless otherwise noted.

² If Sample is 100% Solid hold time is 2 days to extract and 7 days to run

³ Holding time starts from the end of sample collection and ends when analyzed unless otherwise noted.

Oil & Grease	32 oz Glass Jar HCl	28 days	1664A	Liquid
Organochlorine Pesticides	1 Liter Amber None	7 days to extract 40 days to run	608/8081	Liquid
	4 oz Glass Jar None	14 days to extract 40 days to run		Solid
Paint Filter Test	8 oz Glass Jar None	30 days	9095	Liquid/Solid
Percent Oil (% Oil)	4 oz Glass Jar None	365 days	ASTMD 96-98	Liquid/Solid
Percent Water (% Water)	4 oz Glass Jar None	7 days	2540B	Liquid/Solid
PCBs	1 Liter Amber None	7 days to extract 40 days to run	608/8082	Liquid
	4 oz Glass Jar None	14 days to extract 40 days to run		Solid
pH, Corrosivity	125 mL Plastic None	24 hours	4500-H+B	Liquid
	4 oz Glass Jar None	30 days	9045D	Solid
Phenols (Speciated)	1 Liter Amber None	7 days to extract 40 days to run	625/8270C	Liquid
Phenols (Total)	125 mL Amber H ₂ SO ₄	28 days	420.1	Liquid
Phosphorus, Ortho	250 mL Plastic None	48 hours	4500-P E	Liquid
Phosphorus (Total)	250 mL Plastic H ₂ SO ₄	28 days	4500-P E	Liquid
	4 oz Glass Jar None			Solid
Polynuclear Aromatic Hydrocarbons (PNA or PAH)	1 Liter Amber None	7 days to extract 40 days to run	8270C	Liquid
	4 oz Glass Jar None	14 days to extract 40 days to run		Solid
Semi-Volatile Organics (SVOC or BNA)	1 Liter Amber None	7 days to extract 40 days to run	625/8270C	Liquid
	4 oz Glass Jar None	14 days to extract 40 days to run		Solid
Silica	250 mL Plastic None	28 days	4500-Si E	Liquid
SPLP Extraction	32 oz Glass Jar None	14 days	1312	Liquid/Solid
Sulfate	250 mL Plastic None	28 days	300.0	Liquid
Sulfite	250 mL Plastic None	24 hours	4500-SO3 2- B	Liquid
Sulfide (Field Filtered)	125 mL Plastic Zinc Acetate	7 days	4500-S2 D	Liquid
Sulfide (Non-Filtered)	1 Liter Amber None	7 days	4500-S2 D	Liquid
Sulfide (Reactive)	4 oz Glass Jar None	14 days	9030B	Liquid/Solid
TCLP Extraction	32 oz Glass Jar None	14 days ⁴	1311	Liquid/Solid
Total Ash Solids (Ash)	4 oz Glass Jar None	14 days	106.4	Solid
Total Dissolved Solids (TDS)	500 mL Plastic None	7 days	2540C	Liquid
Total Kjeldahl Nitrogen (TKN)	250 mL Plastic H ₂ SO ₄	28 days	4500N(org)/NH3	Liquid
ANALYSIS	BOTTLE TYPE	HOLD TIME⁵	METHOD	MATRIX

⁴ From collection to TCLP Extraction, see solid hold times for requested analyses. From TCLP Extraction to analysis, see liquid hold times for requested analyses.

⁵ Holding time starts from the end of sample collection and ends when analyzed unless otherwise noted.

Total Organic Carbon (TOC)	125 mL Amber H ₂ SO ₄	28 days	5310C	Liquid
Total Petroleum Hydrocarbons (TPH-IR)	32 oz Glass Jar HCl	28 days	418.1	Liquid
Total Solids (TS)	4 oz Glass Jar None	28 days	2540B	Solid
Total Suspended Solids (TSS)/ Volatile Suspended Solids (VSS)	500 mL Plastic None	7 days	2540D	Liquid
Total Volatile Solids (TVS)	4 oz Glass Jar None	7 days	160.4	Solid
TPH Diesel Range Organics (DRO)	1 Liter Amber None	7 days to extract 40 days to run	8015M	Liquid
	4 oz Glass Jar None	14 days to extract 40 days to run		Solid
TPH Gasoline Range Organics (GRO)	2 40 mL VOA HCl	14 days ²	8015M	Liquid
	1 40 mL VOA MeOH			Solid
Turbidity	500 mL Plastic None	48 hours	HACH T.2	Liquid
Viscosity	4 oz Glass Jar None	365 days	ASTM D4212	Liquid
Volatile Organics	2 40 mL VOA HCl	14 days ⁶	624/8260/5035/ 524.2	Liquid
	1 40 mL VOA MeOH			Solid

⁶ Hold time 7 days without HCl preservative

APPENDIX J: OHIO VAP DATA REVIEW CHECKLISTS



EPA OHIO VAP INORGANIC REVIEW CHECK LIST

Sample Delivery Group: _____

Date: _____

INORGANICS	<input checked="" type="checkbox"/>	Checklist Notes
1. ICP/MS Metals Data		
Sequence / Injection Log	<input type="checkbox"/>	_____
Initial Calibration and Calibration Verification	<input type="checkbox"/>	_____
CRDL Standards	<input type="checkbox"/>	_____
Blanks	<input type="checkbox"/>	_____
Interference Check Sample	<input type="checkbox"/>	_____
Spike Sample Recovery	<input type="checkbox"/>	_____
Post-Digest Spike Sample Recovery	<input type="checkbox"/>	_____
Duplicates	<input type="checkbox"/>	_____
Laboratory Control Sample	<input type="checkbox"/>	_____
Analysis Run Log	<input type="checkbox"/>	_____
ICP/MS Tune	<input type="checkbox"/>	_____
Internal Standard Relative Intensity Summary	<input type="checkbox"/>	_____
Linear Ranges	<input type="checkbox"/>	_____
2. Mercury Data		
Sequence / Injection Log	<input type="checkbox"/>	_____
Initial Calibration and Calibration Verification	<input type="checkbox"/>	_____
CRDL Standards	<input type="checkbox"/>	_____
Blanks	<input type="checkbox"/>	_____
Spike Sample Recovery	<input type="checkbox"/>	_____
Post-Digest Spike Sample Recovery	<input type="checkbox"/>	_____
Duplicates	<input type="checkbox"/>	_____
Laboratory Control Sample	<input type="checkbox"/>	_____
Analysis Run Log	<input type="checkbox"/>	_____
3. Cyanide Data		
Bench Sheet - sample and QC sample evaluation	<input type="checkbox"/>	_____
5. Hexavalent Chromium Data		
Bench Sheet - sample and QC sample evaluation	<input type="checkbox"/>	_____
6. Total Solids Data		
Bench Sheet - total solids determination	<input type="checkbox"/>	_____

This data has been reviewed and validated by: _____

APPENDIX J: OHIO VAP DATA REVIEW CHECKLISTS *continued*



EPA OHIO VAP ORGANIC REVIEW CHECK LIST

Sample Delivery Group: _____ Date: _____

ORGANICS	<input checked="" type="checkbox"/>	Checklist Notes
4. Volatiles Data		
<i>a. QC Summary</i>		
Sequence / Injection Log	<input type="checkbox"/>	_____
Surrogate Compound Summary	<input type="checkbox"/>	_____
Matrix Spike/Matrix Spike Duplicate Summary	<input type="checkbox"/>	_____
Method Blank Summary	<input type="checkbox"/>	_____
GC/MS Instrument Performance Check	<input type="checkbox"/>	_____
Internal Standard Area and RT Summary	<input type="checkbox"/>	_____
<i>b. Sample Data</i>		
Manual Integrations	<input type="checkbox"/>	_____
Validated against Merit Integration SOP	<input type="checkbox"/>	_____
<i>c. Standards Data (All Instruments)</i>		
Initial Calibration Data	<input type="checkbox"/>	_____
System Performance/Calibration Check Compounds	<input type="checkbox"/>	_____
5. Semi-Volatiles Data		
<i>a. QC Summary</i>		
Sequence / Injection Log	<input type="checkbox"/>	_____
Surrogate Compound Summary	<input type="checkbox"/>	_____
Matrix Spike/Matrix Spike Duplicate Summary	<input type="checkbox"/>	_____
Method Blank Summary	<input type="checkbox"/>	_____
GC/MS Instrument Performance Check	<input type="checkbox"/>	_____
Internal Standard Area and RT Summary	<input type="checkbox"/>	_____
<i>b. Sample Data</i>		
Manual Integrations	<input type="checkbox"/>	_____
Validated against Merit Integration SOP	<input type="checkbox"/>	_____
<i>c. Standards Data (All Instruments)</i>		
Initial Calibration Data	<input type="checkbox"/>	_____
System Performance/Calibration Check Compounds	<input type="checkbox"/>	_____
6. PCB Data		
<i>a. QC Summary</i>		
Sequence / Injection Log	<input type="checkbox"/>	_____
Surrogate Compound Summary	<input type="checkbox"/>	_____
Matrix Spike/Matrix Spike Duplicate Summary	<input type="checkbox"/>	_____
Method Blank Summary	<input type="checkbox"/>	_____
<i>b. Sample Data</i>		
Manual Integrations Reviewed	<input type="checkbox"/>	_____
<i>c. Standards Data (All Instruments)</i>		
Initial Calibration of Multicomponent Data	<input type="checkbox"/>	_____
Calibration Check Standard	<input type="checkbox"/>	_____

This data has been reviewed and validated by: _____

APPENDIX K: SCHEDULED MAINTENANCE

	Daily	Monthly	Semi Annually	As Needed
Gas Chromatographs - Column changes - Injection port cleaning - Changing septa - Visual observation - Cleaning of detectors	x			x x x x
Gas Chromatograph/Mass Spectrometers - Column changes - Injection port cleaning - Jet separator cleaning - Septum injection port - Visual observation - Changing of rough pump oil - High vacuum pump oil - Changing of oil in turbo pump - Source cleaning - Check vacuum	x x		x x	x x x x x x x
Cold Vapor Analyzer - Cleaning of detector cell - Reaction cell (bubbler) - Replacement of syringe cells - Refill drying tube	x			x x x
Balances - Checked/calibrated			x	
Thermometers - NIST calibrated			x	
Inductively Coupled Plasma/Mass Spectrometer - Changing of rough pump oil - Cone cleaning - Filter cleaning		x	x	x
Air Conditioning - Change carbon filter		x		
Spectrophotometers - Change light				x
Evaporation Station - Change water - Change sensors				x x
De-Ionized Water - Replace ion exchange tank		x		



APPENDIX L: SAMPLE RECEIVING CHECKLIST

MERIT LABORATORY SAMPLE RECEIVING CHECK LIST
2680 EAST LANSING DRIVE, EAST LANSING MI 48823
(517) 332-0167 FAX: (517) 332-6333

Log-in Date: _____ **Logged in by :** _____

Client Info: _____ **Merit ID:** _____

Phone/Fax: _____ **Client Review By:** _____

	Yes	No		Notes
1.	<input type="checkbox"/>	<input type="checkbox"/>	Samples shipped	_____
2.	<input type="checkbox"/>	<input type="checkbox"/>	Samples delivered	_____
3.	<input type="checkbox"/>	<input type="checkbox"/>	Samples left in 24 hr. storage	_____
4.	<input type="checkbox"/>	<input type="checkbox"/>	Are there custody seals/tape or is the drop box locked	_____
5.	<input type="checkbox"/>	<input type="checkbox"/>	Samples are received on ice ($4^{\circ}\text{C} \pm 2^{\circ}\text{C}$) ^[1] Them. #:	_____
6.	<input type="checkbox"/>	<input type="checkbox"/>	Received on ice/Cooling process begun	_____
7.	<input type="checkbox"/>	<input type="checkbox"/>	All bottles intact	_____
8.	<input type="checkbox"/>	<input type="checkbox"/>	Appropriate analytical bottles are used	_____
9.	<input type="checkbox"/>	<input type="checkbox"/>	Merit bottles used	_____
10.	<input type="checkbox"/>	<input type="checkbox"/>	Sufficient sample volume received	_____
11.	<input type="checkbox"/>	<input type="checkbox"/>	Sample(s) require laboratory filtration	_____
12.	<input type="checkbox"/>	<input type="checkbox"/>	Completed pH checks on preserved samples? (No VOAs)	_____
13.	<input type="checkbox"/>	<input type="checkbox"/>	Did any samples need to be preserved in lab?	_____
14.	<input type="checkbox"/>	<input type="checkbox"/>	Do samples have correct chemical preservation?	_____
15.	<input type="checkbox"/>	<input type="checkbox"/>	Sample submitted within holding time	_____
16.	<input type="checkbox"/>	<input type="checkbox"/>	If VOC or TOX bottles, do they contain headspace	_____
17.	<input type="checkbox"/>	<input type="checkbox"/>	COC adequately filled out	_____
18.	<input type="checkbox"/>	<input type="checkbox"/>	COC signed and relinquished to the lab	_____
19.	<input type="checkbox"/>	<input type="checkbox"/>	Sample tag on bottles reflected on COC	_____
20.	<input type="checkbox"/>	<input type="checkbox"/>	Subcontracting needed? Subcontracting to:	_____
21.	<input type="checkbox"/>	<input type="checkbox"/>	Samples on hold	_____

CORRECTIVE ACTION for the above is as follows:

APPLICATION	Corrective Action	Exceptions Present?
Any exceptions	Call the client, notify project manager	

APPENDIX M: MAJOR EQUIPMENT LIST

Merit Laboratories, Inc. Detailed Major Equipment List

Department	Instrument	Description	Qty.	Purchase Date/Serial No.	Analyses (Methods)
Organics	GC/MS	Gas Chromatograph/Mass Spectrometer, Hewlett Packard, GC 5890	2	1998/2716A10642 3118A02391 2716A10847	Volatile Organic Compounds(5035/8260/624)
	GC/MS	Gas Chromatograph/Mass Spectrometer, Agilent, GC 5973/6890N	1	2005/CN10512039-GC US44621405 -MS	Volatile Organic Compounds(5035/8260/624)
	Purge & trap concentrator	Eclipse 4660	3	2005/B450466679P B450466678P	Volatile Prep.
	Purge & trap concentrator	Eclipse 4660	1	2006/D550466457P	Volatile Prep.
	Auto-sampler	Varian, Archon purge & trap auto-sampler system, 51 positions	2	1998/12792 12313	Volatiles
	GC/MS	Gas Chromatograph/Mass Spectrometer, HP, 5890 GC Series II Plus	2	1994/ 3341A01390 3329A00616	Semi-volatile organics/ BNA/Phthalate esters(8270), Phenols(8040)
	MS Detector	Hewlett Packard, 5970 Series Mass Selective Detector, PTE-5, 30m, 1.25mm ID	6	1999/290512037	Volatile Organic Compounds(5035/8260/624)
	Auto-sampler	Hewlett Packard, 7673 Injector, 100 positions	3	2001/3214A30332 3033A23220 3004A20696	Semi-volatile organics/ BNA/Phthalate esters(8270), Phenols(8040)
	Auto-sampler	Varian, Archon purge & trap auto-sampler system, 51 positions	2	2001/1269 12298	Volatiles
	GC	Gas Chromatograph, Varian, Capillary GC 3400 With confirmation column	4	1998/8240 10565 9732 8475	Pesticides(8081), PCBs(8082), Herbicides(8151B)
	GC	Gas Chromatograph, Varian, Capillary GC 3800 With confirmation column	2	2005/06975 11740	Pesticides(8081), PCBs(8082), Herbicides(8151B)
	Auto-sampler	Varian, 48 positions	5	1998/5155 0636 5338 1006 1559	Pesticides(8081), PCBs(8082), Herbicides(8151B)
	HPLC Column	Liquid Chromatography Reverse Phase, Octadecyl Column	1	1991/018356AL	Explosives/ Formaldehyde(8310)
	HPLC Detector	Millipore, Waters 991 Photoiodide Array Detector	1	1992/9910900590	Explosives/ Formaldehyde(8310)
	HPLC Detector	Millipore, Waters Fluorescence Detector	1	1992/470-001095	Explosives/ Formaldehyde(8310)

Merit Laboratories, Inc. Detailed Major Equipment List

Department	Instrument	Description	Qty.	Purchase Date/Serial No.	Analyses (Methods)
Organics	GC/MS	GC/MS Agilent / Auto Sampler 6890/5973/7683B	1	GC-2005/CN10442088 MS-2006/US44621063 Auto-CN44431026	Semi-volatile organics/ BNA/Phthalate esters(8270), Phenols(8040)
	GC/MS	GC/MS, Agilent, GC 5973/6890N	1	MS-2006/US43121018 GC-2006 CN10442131	Volatile Organic Compounds(5035/8260/624)
	HPLC Auto-sampler	Millipore, Waters 715 Ultra Wisp Sampler Processor	1	1992/715-000949	Explosives/ Formaldehyde(8310)
	GC/MS	Hewlett Packard 5890 Series II	1	1999/3121A36026	Semi-volatile organics/ BNA/Phthalate esters(8270), Phenols(8040)
	GC/MS	Agilent Technologies 5975	1	2007/ US55142015	Semi-volatile organics/ BNA/Phthalate esters(8270), Phenols(8040)
	GC/MS/Auto Sampler	Agilent Technologies 7890A/5975B/7683B	1	2008/ MS-U565145582 GC-CN10811101 Auto-CN65242527	Semi-volatile organics/ BNA/Phthalate esters(8270), Phenols(8040)
	GC/MS	Agilent Technologies 7890A/5975B	1	2008/MS-U565145624 GC-CN10733059	Volatile Organic Compounds(5035/8260/624)
	Purge & trap concentrator	Eclipse 4660	1	2005/B450466678P	Volatile Prep.
	Purge & trap concentrator	Eclipse 4660	1	2008/D646466144P	Volatile Prep.
	GC/MS	Agilent Technologies 7890A/5975B	1	2009/ GC-CN10848014 / MS - US81839510	Volatile Organic Compounds in drinking waters (524.2)
	Purge & trap concentrator	Eclipse 4660	1	2009 / E8515466094P	Volatile Organic Compounds in drinking waters (524.2)
	Auto-sampler	Archon 4552	1	2009 / MS0810W001	Volatile Organic Compounds in drinking waters (524.2)

Merit Laboratories, Inc. Detailed Major Equipment List

Department	Instrument	Description	Qty.	Purchase Date/Serial No.	Analyses (Methods)
Inorganics	Spectrophotometer	Hach DR/3000	1	1988/880201476	Chromium VI(218.4/7196), Phosphorus(365.4/365.2), COD(410.4), Turbidity(N/A)
	Spectrophotometer	Hach DR/4000V	1	1999/9906V0000852	MBAS(425.1), Ferrous Iron(315B), Cyanide(335.2), Phenols(420.2), Chloroform(330.5), Silicate(4500-Si), Sulfide(376.2)
	Titration	Hach Digital Titration	2	1988	Alkalinity/Acidity(310.1), Chloride(325.3), Hardness(130.2), Carbon Dioxide(CO2C)
	Conductivity Meter	Hach Conductivity/TDS meter	1	2000/880400761	Conductivity(120.1)
	Carbon Analyzer	Dohrmann, DC-180 Carbon Analyzer	1	2004/RMHJ3599	TOC (415.1)
	Carbon Analyzer	Dohrmann, DC-180 Control Module	1	2004/CMHJ3595	TOC (415.1)
	Ion Chromatograph	Dionex, DX-100 w/ Dionex advanced computer interface	1	1993/ 932107	Ion Chromatography analyses(300.0)
Inorganics	IC auto-sampler	Dionex, auto-sampler, 48 positions	1	1994/ 875015D940201R	
	COD Reactor	Hach COD Reactor	1	1990/880201476	COD(410.4)
	Digestor	Lachat, BD-26 Block Digestor	1	1990/2600-150	Total Kjeldahl Nitrogen(351.4)
	Ammonia electrode	Hach One pH meter w/ ion selective electrode and ammonia membrane module	1	1994/940100023060	Ammonia(350.3), TKN(351.4)
	Dissolved Oxygen Meter	YSI, Model 50	1	1988/380	BOD5/CBOD/Dissolved Oxygen(405.1)
	Dissolved Oxygen Meter	Hach HQ40d	1	2007/1759061200503	BOD5/CBOD/Dissolved Oxygen(10360)
	Stereomicroscope	AO 580 stereomicroscope w/ AO650 60 Hz. light	1	1987	Stereomicroscopic analyses(N/A)
	Discrete Analyzer	DA-3500-Discrete Analyzer Automated Chemistry Analyzer OI Analytical	1	2005/100907E	Colorimetric analysis for Ammonia, phosphorous, Nitrate, Nitrite, Chloride, Sulfide
	Evaporator	Zymark, Turbo Vap II	3	2003/04090 04321	PCB/PNA/BNA/TCLP/TTO/Herbicides extractions(3510)
	Shaker	Glas-Col, 3D Shaker	2	1999/284905 259294	PCB/PNA/BNA/TCLP/TTO/Herbicides(3510), Oil & Grease/TPH(413.1/418.1/1664) extractions
Extractions / FOG / TPH	Oil-In-Water Analyzer	Buck Scientific	1	2001/016	Oil & Grease/TPH (413.1/418.1/1664)
	Sonifier	Branson, Sonifier 450	2	2003/BI90192 BI03108333	PCB/BNA/Herbicides extractions(3550)
	GPC	OI Analytical, Autoprep 2000	1	2005/ D407330629	Dioxin Cleanup for PCBs
	Shaker bath	Lab-Line, Orbit Shaker Bath	1	2000/0599-0531	Formaldehyde extraction(8310)
	Auto-extraction System	Horizon 1000 XL	1	2004/03-1821	Oil & Grease
	Auto-extraction System	Horizon SPE-DEX 3000 Control	1	2004/04-1254	Oil & Grease
	Sonifier	Branson, Sonifier 450	2	2006/B120141	PCB/BNA/Herbicides extractions(3550)
	Evaporator	Zymark, Turbo Vap II	1	2005/TV0524N12355	PCB/PNA/BNA/TCLP/TTO/Herbicides extractions(3510)

Merit Laboratories, Inc. Detailed Major Equipment List

Department	Instrument	Description	Qty.	Purchase Date/Serial No.	Analyses (Methods)
Metals	ICP/MS	Inductively Coupled Plasma/ Mass Spectrometer, HP, ICP/MS 4500 Series Shield Torch System	1	1998/ 3622J00419	ICP/MS Metals (200.8/6020)
	ICP/MS	Inductively Coupled Plasma/ Mass Spectrometer, Perkin Elmer, ICP/MS Elan 5000	1	2004/ P1700403	ICP/MS Metals (200.8/6020)
	ICP/MS	Inductively Coupled Plasma/ Mass Spectrometer, HP, ICP/MS 7500cs Series Octopole Reaction System	1	2007/JPS1201533	ICP/MS Metals (200.8/6020)
	Digestion System	CEM, MDS-81D	1	1997/ 6281-988	
	Digestion System	CEM Marsx	1	2004/XM3128	
	Digestion System	Block Digestor	3	2004/ 3803 3828 3804	
	Cold Vapor Mercury Analyzer	ThermoSeparations, Mercury Monitor 3200	1	1990/ 053678	Cold Vapor Mercury by Atomic Adsorption (245.1/7471)
	Auto Sampler	Thermo Separation Products AutoMetric 3000	1	2004/E1983	Cold Vapor Mercury by Atomic Adsorption (245.1/7471)
	Auto-sampler	ThermoSeparations, Autometric 200 Chromatography Research Supplies, High Pressure Hydrocarbon Trap, Model 300	1	2004/070134ASX	Cold Vapor Mercury by Atomic Adsorption (245.1/7471)
	Cold Vapor Mercury Analyzer	Cetac Quick Trace - Hg Analyzer M-7500	1	2004/120304QTA	Cold Vapor Mercury by Atomic Adsorption (245.1/7471)
TCLP & Waste Analyses	Rotary Extractor	Lars Lande, 5 positions	3	1990/ 1157 1062 1196	TCLP(1311), SPLP(1312)
	Rotary Extractor	Associated Design & MFG. Co Model# 3740-8-BRE	1	1991/1309	TCLP(1311), SPLP(1312)
	pH/ISE Meter	Hach, One Laboratory pH/ISE meter	1	2003/ 030700002265	TCLP(1311), SPLP(1312), pH(950.1/9040)
	Calorimeter	Parr, Oxygen Bomb Calorimeter	1	1990/1341EB BOMB CALORI PLAIN 115/50/60	Halogens/BTU (ASTM 2015)
	Ignition Unit	Parr, Ignition Unit	1	2000/2901 EB Ignition Unit 115/50/60	Halogens/BTU (ASTM 2015)

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Department	Instrument	Description	Qty.	Purchase Date/Serial No.	Analyses (Methods)
		Field Equipment: 2 Field Equipped Vans (GM)			Dissolved Oxygen Meter
		Polysonic Flow Meter			Bailers
		Tripod/Safety Harness			Keck Interface Probe
		14 ISCO Samplers			Solinst Water Level
		2 Monitoring Well Water Level Gauges			Hru Meter
		2 Conductivity/Temperature Meters (in situ)			Neotronics Minigas Monitor
		3 Myron pH/Conductivity Meters			Hand Augers
		COLIWASA			Generator
		Drum Thieves			Filter Flask/Pump
		Monitoring Well Bailers			Hach Field Test Kit
		Soil Auger			Ekman Dredge
		Orion Residual Chloride Meter			Portable Pipe Weirs
		Respirator (Full and Half Face)			Redi-Flow, Grundfos Pump

APPENDIX N: CERTIFICATION SUMMARY TABLE

Analyte	Method	Certification
Inorganics		
Alkalinity	2320B	NY, FL
Ammonia	4500-NH3 D	NY, FL
BOD	10360	NY, FL
Bromide	300.0	NY, FL, MI
Calcium Hardness	2340B	NY
Chloride	300.0	NY, FL
Chromium VI	7196A	NY, FL, OH
COD	410.4	NY, FL
Conductivity	120.1	NY, FL
Corrosivity	9040B	NY, FL
Cyanide	335.4	NY, FL, MI, IN
	335.2	OH
Fluoride	300.0	NY, FL, MI, IN
Hardness	2340C	NY, FL
Nitrate	300.0	MI, IN
Nitrite	300.0	NY, FL, MI, IN
Oil & Grease (Hexane)	1664A	NY, FL
Orthophosphorus	4500-P E	NY, FL
pH	4500-H + B	NY, FL
Phenols (Total)	420.1	NY, FL
Phosphorus	4500-P E	NY, FL
Sulfate	300.0	NY, FL, MI
Sulfide	4500-S D	NY, FL
Temperature	2550B	NY, FL
Total Dissolved Solids	2540C	NY, FL
Total Kjeldahl Nitrogen	4500-NH3 D	NY, FL
Total Organic Carbon	5310C	NY, FL
Total Solids	2540 B	NY, FL
Total Suspended Solids	2540D	NY, FL
Metals		
Aluminum	200.8	NY, FL, OH
	6020	NY, FL, OH
Antimony	200.8	NY, FL, MI, IN
	6020	NY, FL, OH
Arsenic	200.8	NY, FL, MI, IN
	6020	NY, FL, OH
Barium	200.8	NY, FL, MI, IN, OH
	6020	NY, FL, OH
Beryllium	200.8	NY, FL, MI, IN, OH
	6020	NY, FL, OH
Cadmium	200.8	NY, FL, MI, IN, OH
	6020	NY, FL, OH
Calcium	6020	OH
Chromium	200.8	NY, FL, MI, IN, OH
	6020	NY, FL, OH
Cobalt	200.8	NY, FL, OH
	6020	NY, FL, OH
Copper	200.8	NY, FL, MI, IN, OH
	6020	NY, FL, OH
Lead	200.8	NY, FL, MI, IN, OH
	6020	NY, FL, OH
Lead in Dust Wipes	6020	NY
Lead in Paint	6020	NY
Manganese	200.8	NY, FL, OH
	6020	NY, FL, OH

Analyte	Method	Certification
Mercury	245.1	NY, FL, MI, IN
	7470A	OH (Water Only)
	7471A	NY, FL, OH
Molybdenum	200.8	NY, FL
	6020	NY, FL
Nickel	200.8	NY, FL, MI, IN, OH
	6020	NY, FL, OH
Potassium	6020	OH
Selenium	200.8	NY, FL, MI, IN, OH
	6020	NY, FL
Silver	200.8	NY, FL, OH
	6020	NY, FL, OH
Sodium	6020	OH
Strontium	200.8	NY, FL
Thallium	200.8	NY, FL, MI, IN, OH
	6020	NY, FL, OH
Vanadium	200.8	NY, FL, OH
	6020	NY, FL
Zinc	200.8	NY, FL, OH
	6020	NY, FL, OH
PCBs/Pesticides		
4,4'-DDD	8081	NY, FL
4,4'-DDE	8081	NY, FL
4,4'-DDT	8081	NY, FL
Aldrin	8081	NY, FL
alpha-BHC	8081	NY, FL
beta-BHC	8081	NY, FL
Chlordane	8081	NY, FL
delta-BHC	8081	NY, FL
Dieldrin	8081	NY, FL
Endosulfan I	8081	NY, FL
Endosulfan II	8081	NY, FL
Endosulfan sulfate	8081	NY, FL
Endrin	8081	NY, FL
Endrin aldehyde	8081	NY, FL
Heptachlor	8081	FL
Heptachlor epoxide	8081	FL
Lindane	8081	NY, FL
Methoxychlor	8081	NY, FL
PCB-1016	608	NY, FL
	8082	NY, FL
PCB-1221	608	NY, FL
	8082	NY, FL
PCB-1232	608	NY, FL
	8082	NY, FL
PCB-1242	608	NY, FL
	8082	NY, FL
PCB-1248	608	NY, FL
	8082	NY, FL
PCB-1254	608	NY, FL
	8082	NY, FL
PCB-1260	608	NY, FL
	8082	NY, FL
Polychlorinated Biphenyls	8082	OH
Toxaphene	8081	NY, FL
Semi-Volatile Organics		
Semi-Volatile Organic Compounds	8270C	OH

Analyte	Method	Certification
1,2,4-Trichlorobenzene	625	NY, FL
	8270C	NY, FL
2-Chloronaphthalene	625	NY, FL
	8270C	NY, FL
2-Chlorophenol	8270C	NY, FL
2-Methyl-4,6-dinitrophenol	8270C	NY, FL
2-Methylphenol	8270C	NY, FL
2-Nitrophenol	8270C	NY, FL
2,4-Dichlorophenol	8270C	NY, FL
2,4-Dimethylphenol	8270C	NY, FL
2,4-Dinitrophenol	8270C	NY, FL
2,4-Dinitrotoluene	625	NY, FL
	8270C	NY, FL
2,4,5-Trichlorophenol	8270C	NY, FL
2,4,6-Trichlorophenol	8270C	NY, FL
2,6-Dinitrotoluene	625	NY, FL
	8270C	NY, FL
3,3'-Dichlorobenzidine	625	NY, FL
	8270C	NY, FL
4-Bromophenylphenyl ether	625	NY, FL
	8270C	NY, FL
4-Chloro-3-methylphenol	8270C	NY, FL
4-Chlorophenylphenyl ether	625	NY, FL
	8270C	NY, FL
4-Nitrophenol	8270C	NY, FL
Acenaphthene	8270C	NY, FL
Acenaphthylene	8270C	NY, FL
Anthracene	8270C	NY, FL
Benzidine	625	NY, FL
	8270C	NY, FL
Benzo(a)anthracene	8270C	NY, FL
Benzo(a)pyrene	8270C	NY, FL
Benzo(b)fluoranthene	8270C	NY, FL
Benzo(ghi)perylene	8270C	NY, FL
Benzo(k)fluoranthene	8270C	NY, FL
Benzyl butyl phthalate	625	NY, FL
	8270C	NY, FL
Bis(2-chloroisopropyl) ether	625	NY, FL
	8270C	NY, FL
Bis(2-chloroethoxy) methane	625	NY, FL
	8270C	NY, FL
Bis(2-chloroethyl) ether	625	NY, FL
	8270C	NY, FL
Bis(2-ethylhexyl) phthalate	625	NY, FL
	8270C	NY, FL
Cresols, Total	8270C	NY
Chrysene	8270C	NY, FL
Dibenzo(a,h)anthracene	8270C	NY, FL
Diethyl phthalate	625	NY, FL
	8270C	NY, FL
Dimethyl phthalate	625	NY, FL
	8270C	NY, FL
Di-n-butyl phthalate	625	NY, FL
	8270C	NY, FL
Di-n-octyl phthalate	625	NY, FL
	8270C	NY, FL
Fluoranthene	8270C	NY, FL
Fluorene	8270C	NY, FL

Analyte	Method	Certification
Hexachlorobenzene	625	NY, FL
	8270C	NY, FL
Hexachlorobutadiene	625	NY, FL
	8270C	NY, FL
Hexachlorocyclopentadiene	625	NY, FL
	8270C	NY, FL
Hexachloroethane	625	NY, FL
	8270C	NY, FL
Indeno(1,2,3-cd)pyrene	8270C	NY, FL
Isophorone	625	NY, FL
	8270C	NY, FL
Naphthalene	8270C	NY, FL
Nitrobenzene	625	NY, FL
	8270C	NY, FL
N-Nitrosodimethylamine	625	NY, FL
	8270C	NY, FL
N-Nitrosodi-n-propylamine	625	NY, FL
	8270C	NY, FL
N-Nitrosodiphenylamine	625	NY, FL
	8270C	NY, FL
Pentachlorophenol	8270C	NY, FL
Phenanthrene	8270C	NY, FL
Phenol	8270C	NY, FL
Pyrene	8270C	NY, FL
Pyridine	8270C	NY, FL
Diesel Range Organics (DRO)	8015B Modified	NY
Total Petroleum Hydrocarbons DRO	8015B Modified	OH
Volatile Organics		
Volatile Organic Compounds	8260A/8260B	OH
1,1,1-Trichloroethane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
1,1,1,2-Tetrachloroethane	524.2	MI, IN
1,1,2,2-Tetrachloroethane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
1,1,2-Trichloroethane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
1,1-Dichloroethane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
1,1-Dichloroethene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
1,1-Dichloropropene	524.2	MI, IN
1,2-Dichlorobenzene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
1,2-Dichloroethane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
1,2-Dichloropropane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN

Analyte	Method	Certification
1,2,3-Trichlorobenzene	524.2	MI, IN
1,2,3-Trichloropropane	524.2	MI, IN
1,2,4-Trichlorobenzene	524.2	MI, IN
1,2,4-Trimethylbenzene	524.2	MI, IN
1,3-Dichlorobenzene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
1,3-Dichloropropane	524.2	MI, IN
1,3,5-Trimethylbenzene	524.2	MI, IN
1,4-Dichlorobenzene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
2-Butanone (MEK)	8260B	NY, FL
2-Chloroethylvinyl ether	624	NY, FL
	8260B	NY, FL
2-Chlorotoluene	524.2	MI, IN
2,2-Dichloropropane	524.2	MI, IN
4-Chlorotoluene	524.2	MI, IN
Acrolein	624	NY, FL
	8260B	NY, FL
Acrylonitrile	624	NY, FL
	8260B	NY, FL
Benzene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Benzyl chloride	8260B	NY, FL
Bromobenzene	524.2	MI, IN
Bromochloromethane	524.2	MI, IN
Bromodichloromethane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Bromoform	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Bromomethane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Carbon tetrachloride	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Chlorobenzene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Chloroethane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Chloroform	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Chloromethane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
cis-1,2-Dichloroethene	524.2	MI, IN
cis-1,3-Dichloropropene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Dibromochloromethane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Dibromomethane	524.2	MI, IN

Analyte	Method	Certification
Dichlorodifluoromethane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Ethyl benzene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Hexachlorobutadiene	524.2	MI, IN
Isopropylbenzene	524.2	MI, IN
Methylene chloride	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Naphthalene	524.2	MI, IN
n-Butylbenzene	524.2	MI, IN
n-Propylbenzene	524.2	MI, IN
o-Xylene	524.2	MI, IN
p-Isopropyltoluene	524.2	MI, IN
p,m-Xylene	524.2	MI, IN
sec-Butylbenzene	524.2	MI, IN
Styrene	524.2	MI, IN
tert-Butylbenzene	524.2	MI, IN
tert-Methyl butyl ether (MTBE)	524.2	MI, IN
Tetrachloroethene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Toluene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
trans-1,2-Dichloroethene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
trans-1,3-Dichloropropene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Trichloroethene	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Trichlorofluoromethane	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Vinyl chloride	624	NY, FL
	8260B	NY, FL
	524.2	MI, IN
Xylenes (Total)	624	NY, FL
	8260B	NY, FL
Gasoline Range Organics (GRO)	8015B Modified	NY, IN
Total Petroleum Hydrocarbons GRO	8015 B Modified	OH
Other		
TCLP Extraction	1311	NY

NY: NY NELAC Certification #11814
FL: FL NELAC Certification #E871045
MI: MI Drinking Water Certification #9956
IN: IN Drinking Water Certification #C-MI-07
OH: OHIO VAP Certification #CL0002

WBE: Women's Business Enterprise Certification #2005110032
Certifications as of June 2010
Please contact the laboratory for up-to-date certifications

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METHOD 8260B (VOCs) / 8015M (GRO)/8260SIM^[1]

1.0 SCOPE AND APPLICATION

- 1.1 This sop is used to determine volatile organic compounds in a variety of matrices. This sop is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mounds, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. See Table 1 for a list of compounds (along with their characteristic ions) that have been evaluated.
- 1.2 This sop is also used for the analysis of petroleum hydrocarbons, including gasoline range organics (GROs). GROs correspond to the range of alkanes from C₆ to C₁₀ but are not restricted to this range and covering a boiling point range of approximately 60°C - 170°C. The identification of specific fuel types may be complicated by environmental processes such as evaporation, biodegradation, or when more than one fuel type is present.
- 1.3 There are various techniques by which these compounds may be introduced into the GC/MS system. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid, waste, and oil samples), is the most commonly used technique for volatile organic analytes. Method 5000 provides general information on the selection of other introduction methods.
- 1.4 The practical quantitation limit (PQL) of this sop for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrupole instrumentation and the purge-and-trap technique, limits should be approximately 50 µg/kg (wet weight) for solid samples and 1 µg/L for ground water (see Table 2a). When lower RDLs are required, the mass spectrometer (MS) can be set to selective ion monitoring (SIM) to achieve limits approximately 20 times lower than obtainable using the full scan method. The practical quantitation limit (PQL) of GROs is approximately 5 mg/kg (wet weight) for soil/sediment samples and is 0.2 mg/L for ground water samples (see Table 2b). Regardless of the sample matrix, PQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.
- 1.5 This sop is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.
- 1.6 This SOP is not for use with samples that come into the lab for OHIO VAP work.

2.0 SUMMARY OF METHOD

- 2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other methods. The analytes are introduced directly to a wide-bore capillary column. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).
- 2.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point (or more) calibration curve.
- 2.3 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

^[1] The SIM analysis is applicable for MDEQ low RDL level analytes.

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3.0 INTERFERENCES

- 3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. Blank values are not subtracted from sample results.
- 3.2 Cross-contamination may occur when any sample is analyzed immediately after a sample containing high concentrations of volatile organic compounds. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to allow the system to be cleaned as well as to demonstrate the ultimate absence of cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

- 4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.
- 4.1.2 20 m × 0.18 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 1-μm film thickness, or equivalent.
- 4.1.3 Mass spectrometer capable of scanning from 35 to 200 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-bromofluorobenzene (BFB) which meets the criteria in Table 5.
- 4.1.4 GC/MS interface - The capillary column is interfaced through a direct connection to the GC/MS system.
- 4.1.5 Data system - A computer system is interfaced to the mass spectrometer. Hewlett-Packard Chemstation software (with environmental data analysis) is used to acquire and process GC/MS data.

4.2 Purge-and-trap device.

4.3 Microsyringes - 2 to 500-μL.

4.4 Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

4.5 Glass bottles - 40-mL, with PTFE-lined screw-caps.

5.0 REAGENTS

- 5.1 Reagent grade inorganic chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without introducing adverse interferences.
- 5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water.
- 5.3 Stock standard solutions
 - 5.3.1 Certified stock standard solutions are purchased when available for the bulk of desired analytes. They are typically available at concentrations of 1000 to 2000 mg/L.
 - 5.3.2 Supplemental compounds added to calibration mixes are generally prepared gravimetrically from neat standard references (in order to create a high-concentration stock solution).

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- 5.3.3 Stock standard solutions are stored in bottles with PTFE-lined screw-caps. They are refrigerated and protected from light, as recommended by the standard manufacturer.
- 5.3.4 Neat standard references are used in order to create a stock solution ~10000 mg/L for GRO standards.
- 5.3.5 Stock standard solutions are replaced prior to expiration, or sooner if comparison with quality control check samples indicates a problem.
- 5.4 Internal standard solutions - The internal standards used are pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d₅, and 1,4-dichlorobenzene-d₄ (see Table 3). Internal standards are used at a working concentration of 25 mg/L and are added to samples, spikes, blanks, and calibration standards at a uniform concentration of 50 µg/L (i.e. 10µL per 5000µL purge volume). For SIM (selective ion monitoring) analysis, internal standards are the same, but with concentrations at 0.1 ppb (µg/L).
- 5.5 Calibration standards - A minimum of five calibration standards are prepared at different concentrations. The lowest calibration standard corresponds to a sample concentration at or below the standard reporting limit. The remaining standards should represent the working range of the GC/MS system. Each standard should contain each analyte for quantitation by this method.
- 5.6 Surrogate standards - The surrogates used are toluene-d₈, 4-bromofluorobenzene, and 1,2-dichloroethane-d₄. Surrogate standards are used at a working concentration of 25 mg/L and are added to samples, spikes, blanks, and calibration standards at a uniform concentration of 50 µg/L, or less.). For SIM (selective ion monitoring) analysis, surrogate standards are the same, but with concentrations at 0.1 ppb (µg/L).
- 5.7 Matrix spike and laboratory control standards - Matrix spiking solutions are prepared using stock solutions from a different vendor, relative to those used for calibration, where possible. The standards contain nearly the same list of compounds as those in the calibration standards. In any event, the matrix spike includes the minimally required compounds 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene.
 - 5.1.1 Matrix spiking mixes for individual analytes are created at 100 mg/L and spiked into samples at 50 µg/L (i.e. 2.50µL per 5000µL purge volume).
 - 5.1.2 For SIM (selective ion monitoring) analysis, compounds of interest are spiked at concentrations of 0.1 ppb (µg/L).
 - 5.1.3 The matrix spiking mix for GRO is created at 10000 mg/L and spiked into samples at 1000 µg/L (i.e. 0.5µL per 5000µL purge volume).
- 5.8 Methanol, CH₃OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.
- 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING
 - 6.1 Unanalyzed samples are refrigerated in sealed vials.
 - 6.2 Samples and target compound standards are refrigerated and stored separately.
 - 6.3 Holding times for analysis depend on the sample type, method of collection, and type of preservation. See Method 5030B/5035 (SOP#075035) for details.
- 7.0 PROCEDURE
 - 7.1 Sample introduction.
 - 7.1.1 Direct injection - This method of introduction is used only rarely, generally when the compounds of interest exhibit poor purging efficiency. Quantitation in this case, if required, is generally subject to external standard calibration procedures (cf. Method 8000).

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- 7.1.2 Purge-and-trap - This is the normal means of sample introduction for both soil and water samples. All samples, standards, spikes, and blanks are introduced into the GC/MS system in an identical manner (see Merit SOP#075035).
- 7.2 GC/MS operating conditions - see Table 4 for routine operating conditions for VOA analysis
 - 7.2.1 For selective ion monitoring (SIM), the mass spec is put into the selective ion monitoring mode. Based on compounds of interest, the time windows are set within the run (i.e. for internal standards, surrogate standards, compounds). For each time window, corresponding to a compound, including internal and surrogate standards, a minimum of 3 ions are chosen for qualitative analysis. One ion (primary ion), generally the most abundant ion is used for quantitative analysis.
- 7.3 Initial calibration
 - 7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 5 for 4-bromofluorobenzene. Analyses does not begin until these criteria are met.
 - 7.3.1.1 In the absence of any other manipulations, evaluate the mass spectrum of the peak apex or the scan immediately preceding or following from the total ion chromatogram for the BFB peak. This is the default approach used.
 - 7.3.1.2 If the above evaluation is adversely affected by ion peak asymmetry, average the three highest intensity scans of the peak or average the mass spectrum ranging from the 10% initial peak intensity to the tailing 10% peak intensity level from the total ion chromatogram for the BFB peak.
 - 7.3.1.3 If the above evaluation is adversely affected by background contamination, perform a background subtraction with a spectrum within 20 scans of the BFB peak which does not represent a target compound. Use of this procedure may be indicative of failing MS performance. The MS source should be cleaned and re-tuned.
 - 7.3.1.4 The BFB mass intensity criteria in Table 5 are used as tuning acceptance criteria.
 - 7.3.1.5 All subsequent standards, samples, MS/MSDs, and blanks associated with a BFB analysis must use the identical mass spectrometer instrument conditions, Exception: for selective ion monitoring (SIM), tune is run using full scan acquisition and subsequent samples are acquired using selective ion monitoring (SIM).
 - 7.3.2 Purge and analyze each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Table 1). A set of at least five calibration standards is necessary. The purge volume must be the same for all standards and sample extracts. Table 6 details the dilutions necessary to create a set of calibration standards. Figure 1 shows a chromatogram of a midpoint calibration standard.
 - 7.3.3 Calculate response factors (RF s) for each target analyte relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the areas of the standard compound and corresponding internal standard, respectively. likewise, C_s and C_i are the respective concentrations (in any consistent set of units) of the standard compound and corresponding internal standard.
 - 7.3.4 System performance check compounds (SPCCs)
 - 7.3.4.1 A system performance check must be performed to ensure that minimum RF s are met before the calibration curve is used. For volatiles, the System Performance Check Compounds (SPCCs) are: chloromethane, 1,1-dichloroethane, bromoform, chlorobenzene, and 1,1,2,2-tetrachloroethane. (cf. Table 3). No response factor criteria are applied to selective monitoring SIM analysis,
 - 7.3.4.2 The minimum acceptable average RF for these compounds is 0.1 (for chloromethane, 1,1-dichloroethane, and bromoform) and 0.3 (for chlorobenzene and 1,1,2,2-tetrachloroethane). These SPCCs typically have low RF s and tend to decrease

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in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

- 7.3.4.3 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, contamination in the purge-and-trap system, excessively high or low purge flow rates, and active sites in the column or chromatographic system. Replacing the calibration standards, clipping and/or replacing the column will likely solve this problem.
- 7.3.5 Calibration check compounds (CCCs)
- 7.3.5.1 The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is in addition to the successful calibration of the target analytes using one of the approaches described in Section 7.0 of Method 8000.
- 7.3.5.2 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual CCC compound (1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride; see Table 3) must be less than or equal to 30%.
- 7.3.5.3 If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.
- 7.3.6 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. This is accomplished by setting the retention time extraction windows in the Chemstation software.
- 7.3.7 Linearity of target analytes - If the %RSD of any target analytes is 15% or less, then the relative response factor may be assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation.
- 7.3.7.1 Refer to Method 8000 if a least-squares regression is used to determine a linear or quadratic fit to the calibration data. Note that quadratic polynomials are generally fit through the origin in order to prevent the symptomatic aphysical prediction of high concentrations at very low responses. . In any event, the COD for any regression fit should be ≥ 0.99 . In addition, 6 calibration data points are required for a calibration fit with 3 free parameters, while 5 are required for a calibration fit with 1 or 2 free parameters.
- 7.3.7.2 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, *etc.*
- 7.3.7.3 The quality of the calibration fit for any particular compound is communicated to the data user via the Quality Control report for a given batch of samples. The calibration summary report includes: the concentration and RF for each standard in the calibration curve, the type of calibration fit, the calibration fit parameters (*i.e.* average RF or regression coefficients), and the appropriate calibration quality metric (*i.e.* %RSD or COD).
- 7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

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- 7.4.1 Prior to the analysis of samples or calibration standards, purge the BFB standard into the GC/MS system. The resultant mass spectrum for BFB must meet the criteria given in Table 5 before sample analysis begins. These must be *injected* within 12 hours of the injection time for the BFB.
- 7.4.2 The initial calibration for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC/MS (50 µg/L; this represents 2.50 µL of the 100 mg/L calibration standard solution in a 5mL purge volume). A concentration of 0.1µg/L is analyzed for selective ion monitoring (SIM) procedures. The results from the calibration standard analysis must meet the verification acceptance criteria provided below for the SPCC and CCC compounds.
- 7.4.3 A method blank is run every 20 samples to ensure that the total system (preparation glassware, introduction device, transfer lines, and the GC/MS system itself) is free of contaminants. A method blank/wash sample is also run after calibration check/spike samples and prior to analytical samples in order to eliminate carryover contamination from the purge-and-trap system.
- 7.4.4 System performance check compounds (SPCCs)
 - 7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC in the calibration verification standard must meet the minimum response factors given above. This is the same check that is applied during the initial calibration (see §7.3.4.2).
 - 7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins.
- 7.4.5 Calibration check compounds (CCCs)
 - 7.3.5.1 After the system performance check is met, the CCCs listed in Table 3 are used to check the validity of the initial calibration. Percent drift is used to evaluate the CCC response and it must be ≤20%.
 - 7.3.5.2 If the percent drift for each CCC is ≤20%, then the initial calibration is assumed to be valid. If the criterion is not met for any one CCC, then corrective action must be taken prior to the analysis of samples (see previous). Drift is defined as the normalized deviation of the measured from the spike value of a target component:
$$\%D = \left| \frac{C - C_{spike}}{C_{spike}} \right| \cdot 100$$
 - 7.3.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins.
- 7.5 GC/MS analysis of samples
 - 7.5.1 Samples are screened at a diluted state via GC/MS whenever possible prior to analysis within a 12-hour QC batch. This can identify potentially low surrogate recoveries, high target compound concentrations, non-target matrix interferences. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.
 - 7.5.2 Use a 5 mL syringe to take a 5 mL aliquot from the sample vial. Be sure to eliminate any air bubbles from within the syringe. Table 6 has a list of commonly used dilutions as well as the required amount of sample, water, and internal standard for each dilution.
 - 7.5.3 Add 10 µL of 25 mg/L internal/surrogate standard mixture to each sample. If the sample also represents a matrix spike, add 2.50 µL of 100 mg/L target compound matrix spiking mixture to the sample (or 0.5µL of the 10000 mg/L GRO spiking mixture, as appropriate). For SIM analysis, internal and surrogate standards are spiked at 0.1µg/L.

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- 7.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract should be diluted and reanalyzed. In any event, a result based on an extrapolation of calibration curve beyond the working range is flagged on the analytical report.
- 7.5.5 The Extracted Ion Current Profile (EICP) area for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. Changes by more than a factor of two (*i.e.* 50% to 200%) can indicate adverse matrix effects (in the case of an isolated sample) or degrading MS performance (in the case of a systematic low bias). A single-sample matrix effect is documented either via screening or re-analysis and is noted on the analytical report (see Table 7). Similarly, the retention times for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. The change in retention time for any internal standard by more than 30 seconds of the most recent calibration verification standard is indicative of the same potential problems listed above and should be flagged/corrected as appropriate.
- 7.6 Qualitative analysis
- 7.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are given in Tables 1a and 1b. Compounds are identified when the following criteria are met.
- 7.6.1.1 Initial selection of a target compound peak is performed by the Chemstation data system search routine. The search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time.
- 7.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component. This is accomplished using retention time extraction windows within the Chemstation data system.
- 7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)
- 7.6.1.4 Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.
- 7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (*i.e.*, a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.
- 7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (*i.e.*, only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.
- 7.6.1.7 In the two previous cases, analyst expertise as well as knowledge of site history may be important in accepting/rejecting the identification of a compound. In the event of

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continued uncertainty, the analyst should preferentially make a conservative judgement and accept an identified hit, allowing the potential for a false positive.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:

- Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
- The relative intensities of the major ions should agree within $\pm 20\%$.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.

7.7.2 The curve fit applied in the initial calibration is the same as that used to compute the concentration of a target analyte in a sample. All curve fits are evaluated by the data system and are of the form: $A_s/A_i = k_0 + k_1[C_s/C_i] + k_2[C_s/C_i]^2$. Here A_s and A_i are the areas of the target and internal standard, C_s and C_i are the concentrations of the target and internal standard, and k_i is the i^{th} -order regression coefficient. Note that for a mean RF fit to the calibration data, $k_1 \equiv \langle \text{RF} \rangle$, while $k_0, k_2 \equiv 0$.

7.7.3 The concentration of any non-target analytes identified in the sample may be estimated by assuming a mean RF of 1 and by using the TIC areas for the nearest internal standard and target compound. The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.7.4 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Otherwise, structural isomers are quantitated as isomeric pairs (such as p- and m-xylene).

7.8 Special procedures for gasoline range organics (GROs) - The following items detail the differences in the calibration procedures for multicomponent, gasoline range organics from the general, single component procedures outlined above.

7.8.1 A set of at least five calibration standards per §7.2 and §7.3.2. Figure 2 represents a GRO chromatogram.

7.8.2 The measured response from the TIC is used to represent the GRO calibration with an internal standard calibration.

7.8.3 Calculate the response factor (RF) for the TIC relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the area of the TIC and characteristic mass over its respective time range and corresponding internal standard, respectively. Likewise, C_s and C_i are the respective concentrations (in any consistent set of units) of the *total fuel* and corresponding internal standard. The characteristic time ranges for each mass depend upon current

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chromatographic conditions. The time ranges used for the sample chromatograms in Figures 1 and 2 are listed in the respective figure.

The relative area response vs. relative concentration for the TIC and characteristic mass is calibrated in the same manner as described in §7.3.7 and §7.7.

- 7.8.4 In addition to the routine SPCC/CCC check standard, a GRO check standard is analyzed in order to characterize the efficiency of the present GRO calibration in terms of recovery and retention times.

8.0 QUALITY CONTROL

- 8.1 All of the quality control items employed and evaluated are listed in Table 7. In addition, the table indicates the frequency of each QC item along with appropriate courses of corrective action.
- 8.2 Control limits for surrogate and matrix spikes are listed in Table 9.
- 8.3 Quality control items are inspected by the analyst as the data becomes available. At the conclusion of the analytical batch, all of the samples, spikes, standards, *etc.* are processed and evaluated automatically and stored electronically for future reference/retrieval.

9.0 METHOD PERFORMANCE

- 9.1 Laboratory-specific performance data is provided in this document
- 9.2 Table 2a and 2b present the results for detection limit studies. The MDL, PQL and ratio of PQL/MDL is given for each analyte in the target compound list.
- 9.3 Table 9 presents the lower and upper acceptance limits for all surrogate and matrix spiking compounds.

10.0 REFERENCES

1. SW-846, 1996, Revision 3; Methods 3500, 3510, 3550, 8000, 8015, 8260, 624.

11.0 SAFETY

- 11.1 Eye protection and gloves must be worn while performing Volatile analyses.
- 11.2 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 11.3 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
- 11.4 A reference file of material safety data sheets (MSDSs) is available to all personnel.
- 11.5 Specific attention be paid (but not limited) to
- 11.5.1 Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.
- 11.5.2 Methanol may react violently with acids, acid chlorides, acid anhydrides, oxidizing agents, reducing agents and alkali metals. Protect from moisture. Highly flammable.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

- 12.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.

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12.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 APPROVAL AND ISSUE

13.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

Analyst	Date
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Andy Ball, QA Officer	Date
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Maya V. Murshak, Technical Director	Date
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14.0 TABLES AND FIGURES

Table 1. Summary of Retention Times[†] and Characteristic Ions for Volatile Organics

Table 2a. Summary of Practical Quantitation Limits for Volatile Organics

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Table 5. BFB Tune Evaluation Criteria

Table 6. Commonly Used Dilutions for Sample Preparation

Table 7. Quality Control Items, Frequency, and Corrective Action

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Figure 1. Example Total Ion Chromatogram for a Midpoint Volatile Calibration Standard[†]

Figure 2. Example Total Ion Chromatogram for a Gasoline Range Organics Calibration Standard[†]

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Table 1. Summary of Retention Times[†] and Characteristic Ions for Volatile Organics

#	Compound	t _R (min)	t _R /t _{R,I} (-)	t _R -t _{R,I} (min)	1 ⁰ m/z	2 ⁰ m/z	3 ⁰ m/z	4 ⁰ m/z
1)	PENTAFLUOROBENZENE	3.58	1.000	0.00	168	99	37	
2)	1,2-DICHLOROETHANE-D4	3.8	1.061	0.22	65	102	104	
3)	1,1,2-Trichloro-1,2,2-trif	1.9	0.531	-1.68	101	151	103	
4)	Diethyl ether (*)	1.7	0.475	-1.88	74	59	45	
5)	Acetone (*)	1.89	0.528	-1.69	58	43	44	
6)	Methyl iodide (iodomethane)	1.97	0.550	-1.61	142	141	127	
7)	Carbon disulfide (*)	2.01	0.561	-1.57	76	78	44	
8)	Methyl Acetate	2.09	0.584	-1.49	43	74	59	
9)	tert-Methyl butyl ether (M	2.37	0.662	-1.21	73	57	41	43
10)	Acrylonitrile (*)	2.39	0.668	-1.19	52	53	54	
11)	2-Butanone (MEK) (*)	3.23	0.902	-0.35	43	72	57	
12)	Dichlorodifluoromethane	1.17	0.327	-2.41	85	87	50	
13)	Chloromethane (SPCC)	1.25	0.349	-2.33	50	52	49	
14)	Vinyl Chloride (CCC)	1.32	0.369	-2.26	62	64	61	
15)	Bromomethane	1.44	0.402	-2.14	94	96	81	
16)	Chloroethane	1.46	0.408	-2.12	64	66	49	51
17)	Acrolein	1.82	0.508	-1.76	56	55	53	
18)	Trichlorofluoromethane	1.66	0.464	-1.92	101	103	66	105
19)	1,1-Dichloroethene (CCC/MS	1.86	0.520	-1.72	61	96	63	98
20)	Methylene Chloride	2.19	0.612	-1.39	84	49	86	51
21)	trans-1,2-Dichloroethene	2.38	0.665	-1.20	61	96	63	98
22)	1,1-Dichloroethane (SPCC)	2.73	0.763	-0.85	63	65	83	
23)	cis-1,2-Dichloroethene	3.21	0.897	-0.37	96	61	98	
24)	Tetrahydrofuran	3.42	0.955	-0.16	42	41	71	
25)	Chloroform (CCC)	3.46	0.966	-0.12	83	85	47	
26)	Bromochloromethane	3.4	0.950	-0.18	130	49	93	128
27)	1,1,1-Trichloroethane	3.57	0.997	-0.01	97	99	61	
28)	1,1-Dichloropropene	3.67	1.025	0.09	75	77	110	
29)	Cyclohexane	3.63	1.014	0.05	56	84	41	
30)	1,4-DIFLUOROBENZENE	4.07	1.000	0.00	114	88	57	
31)	TOLUENE-D8	4.95	1.216	0.88	98	100	70	
32)	4-Methyl-2-pentanone (MIBK	4.9	1.204	0.83	58	85	100	43
33)	2-Hexanone (*)	5.37	1.319	1.30	58	43	85	100
34)	2-chloroethylvinyl ether	4.73	1.162	0.66	63	106	65	
35)	Carbon Tetrachloride	3.67	0.902	-0.40	117	119	121	
36)	Benzene (MS)	3.82	0.939	-0.25	78	77	51	
37)	1,2-Dichloroethane	3.85	0.946	-0.22	62	98	100	64
38)	Trichloroethene (MS)	4.23	1.039	0.16	95	132	130	134
39)	1,2-Dichloropropane (CCC)	4.38	1.076	0.31	63	76	62	
40)	Bromodichloromethane	4.56	1.120	0.49	83	85	127	129
41)	Methyl Cyclohexane	4.33	1.064	0.26	55	83	41	98
42)	Dibromomethane	4.47	1.098	0.40	174	93	172	79
43)	cis-1,3-Dichloropropene	4.82	1.184	0.75	75	77	110	
44)	Toluene (CCC/MS)	4.99	1.226	0.92	91	92	65	
45)	trans-1,3-Dichloropropene	5.13	1.260	1.06	75	110	77	
46)	1,1,2-Trichloroethane	5.24	1.287	1.17	83	97	99	85

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#	Compound	t_R (min)	$t_R/t_{R,I}$ (-)	$t_R - t_{R,I}$ (min)	$1^0 m/z$	$2^0 m/z$	$3^0 m/z$	$4^0 m/z$
47)	Tetrachloroethene	5.29	1.300	1.22	166	129	164	
48)	CHLOROBENZENE-D5	5.76	1.000	0.00	82	117	119	
49)	4-BROMOFLUOROBENZENE	6.38	1.108	0.62	174	95	176	
50)	trans-1,4-Dichloro-2-buten	6.49	1.127	0.73	53	89	124	75
51)	Dibromochloromethane	5.46	0.948	-0.30	129	127	79	
52)	1,2-Dibromoethane	5.52	0.958	-0.24	107	109	81	
53)	Chlorobenzene (SPCC/MS)	5.77	1.002	0.01	112	77	114	
54)	1,1,1,2-Tetrachloroethane	5.82	1.010	0.06	131	133	117	119
55)	Ethylbenzene (CCC)	5.82	1.010	0.06	91	106	77	
56)	p,m-Xylene	5.88	1.021	0.12	106	91	77	
57)	o-Xylene	6.09	1.057	0.33	91	106	77	
58)	Styrene	6.1	1.059	0.34	104	78	103	
59)	Isopropylbenzene	6.28	1.090	0.52	105	120	77	
60)	Bromoform (SPCC)	6.23	1.082	0.47	173	171	175	
61)	1,1,2,2-Tetrachloroethane	6.47	1.123	0.71	83	85	131	133
62)	1,2,3-Trichloropropane	6.49	1.127	0.73	110	75	97	61
63)	n-Propylbenzene	6.5	1.128	0.74	91	120	105	
64)	Bromobenzene	6.46	1.122	0.70	156	77	158	
65)	1,3,5-Trimethylbenzene	6.59	1.144	0.83	120	105	77	
66)	tert-Butylbenzene	6.76	1.174	1.00	91	119	134	
67)	1,2,4-Trimethylbenzene	6.79	1.179	1.03	120	105	77	
68)	1,4-DICHLOROBENZENE-D4	6.99	1.000	0.00	152	150	115	
69)	sec-Butylbenzene	6.87	0.983	-0.12	105	134	91	
70)	p-Isopropyltoluene	6.95	0.994	-0.04	119	91	134	
71)	1,3-Dichlorobenzene	6.95	0.994	-0.04	146	148	111	
72)	1,4-Dichlorobenzene	7	1.001	0.01	146	148	111	
73)	1,2-Dichlorobenzene	7.2	1.030	0.21	146	148	111	
74)	1,2,3-Trimethylbenzene	7.01	1.003	0.02	105	120	77	
75)	n-Butylbenzene	7.16	1.024	0.17	91	92	134	
76)	Hexachloroethane	7.32	1.047	0.33	201	117	166	
77)	1,2-Dibromo-3-Chloropropan	7.61	1.089	0.62	157	155	75	159
78)	1,2,4-Trichlorobenzene	8.02	1.147	1.03	182	180	145	109
79)	Hexachlorobutadiene	8.09	1.157	1.10	225	227	223	190
80)	1,2,3-Trichlorobenzene	8.27	1.183	1.28	180	182	145	109
81)	Naphthalene	8.15	1.166	1.16	128	102	127	129
82)	2-Methylnaphthalene	8.72	1.247	1.73	142	141	115	

†: Absolute retention times (t_R) listed are from calibration FT060808.M. Absolute and relative retention times ($t_R/t_{R,I}$) may shift with the present condition of the column (*i.e.* new, clipped, *etc.*), but the differential retention times ($t_R - t_{R,I}$) tend to remain constant given the same chromatographic temperature program.

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Table 2a. Summary of Practical Quantitation Limits for Volatile Organics[†]

Compound	Water Matrix			Soil Matrix		
	PQL _w (ug/l)	MDL _w (ug/l)	P/M _w (-)	PQLs (ug/l)	MDLs (ug/l)	P/Ms (-)
1,1,2-Trichloro-1,2,2-trif	1	0.2	6.3	50	8.9	5.6
Diethyl ether (*)	1	0.3	3.2	50	13.3	3.8
Acetone (*)	10	4.0	2.5	500	126.0	4.0
Methyl iodide (iodomethane)	1	0.1	12.3	50	6.0	8.4
Carbon disulfide (*)	1	0.1	11.3	50	9.6	5.2
Methyl Acetate	1	0.3	3.5	50	35.1	1.4
tert-Methyl butyl ether (M	1	0.1	12.4	50	5.3	9.5
Acrylonitrile (*)	1	0.4	2.4	50	14.1	3.6
2-Butanone (MEK) (*)	10	1.4	7.2	500	53.6	9.3
Dichlorodifluoromethane	1	0.3	3.9	50	9.0	5.6
Chloromethane (SPCC)	1	0.2	6.2	50	6.1	8.2
Vinyl Chloride (CCC)	1	0.2	4.1	50	6.2	8.0
Bromomethane	1	0.4	2.7	50	12.6	4.0
Chloroethane	1	0.2	5.3	50	11.3	4.4
Acrolein	10	0.9	10.6	500	46.1	10.8
Trichlorofluoromethane	1	0.1	10.8	50	7.1	7.1
1,1-Dichloroethene (CCC/MS	1	0.1	8.4	50	7.6	6.6
Methylene Chloride	1	0.2	4.6	50	7.9	6.3
trans-1,2-Dichloroethene	1	0.1	15.9	50	6.3	7.9
1,1-Dichloroethane (SPCC)	1	0.1	9.6	50	4.9	10.3
cis-1,2-Dichloroethene	1	0.1	8.5	50	3.6	13.9
Tetrahydrofuran	10	1.2	8.6	500	34.1	14.7
Chloroform (CCC)	1	0.1	11.5	50	5.3	9.4
Bromochloromethane	1	0.2	5.3	50	12.7	3.9
1,1,1-Trichloroethane	1	0.1	9.8	50	3.8	13.1
1,1-Dichloropropene	1	0.1	8.5	50	4.8	10.5
Cyclohexane	1	0.1	7.5	50	5.7	8.7
4-Methyl-2-pentanone (MIBK	10	0.1	68.2	500	11.2	44.7
2-Hexanone (*)	10	0.3	30.9	500	17.0	29.5
2-chloroethylvinyl ether	1	0.1	8.4	50	9.5	5.3
Carbon Tetrachloride	1	0.1	7.7	50	2.8	18.0
Benzene (MS)	1	0.1	18.5	50	4.6	10.9
1,2-Dichloroethane	1	0.2	4.5	50	4.9	10.2
Trichloroethene (MS)	1	0.2	6.6	50	9.1	5.5
1,2-Dichloropropane (CCC)	1	0.1	11.2	50	7.4	6.8
Bromodichloromethane	1	0.2	5.1	50	4.8	10.5
Methyl Cyclohexane	1	0.2	5.4	50	6.0	8.3
Dibromomethane	1	0.2	5.2	50	9.2	5.4
cis-1,3-Dichloropropene	1	0.1	8.1	50	2.6	19.0
Toluene (CCC/MS)	1	0.1	14.4	50	3.5	14.4
trans-1,3-Dichloropropene	1	0.1	8.2	50	5.6	8.9
1,1,2-Trichloroethane	1	0.2	4.1	50	8.2	6.1
Compound	Water Matrix			Soil Matrix		

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	PQL _w (ug/l)	MDL _w (ug/l)	P/M _w (-)	PQL _s (ug/l)	MDL _s (ug/l)	P/M _s (-)
Tetrachloroethene	1	0.1	13.2	50	25.7	1.9
trans-1,4-Dichloro-2-buten	1	0.3	3.8	50	14.3	3.5
Dibromochloromethane	1	0.2	5.5	50	7.5	6.7
1,2-Dibromoethane	1	0.2	5.8	50	2.7	18.5
Chlorobenzene (SPCC/MS)	1	0.1	16.7	50	4.4	11.4
1,1,1,2-Tetrachloroethane	1	0.1	7.3	50	7.5	6.6
Ethylbenzene (CCC)	1	0.1	11.3	50	3.1	16.3
p,m-Xylene	1	0.1	8.4	50	5.3	9.4
o-Xylene	1	0.1	8.6	50	3.4	14.9
Styrene	1	0.1	16.0	50	4.0	12.4
Isopropylbenzene	1	0.1	10.9	50	4.4	11.3
Bromoform (SPCC)	1	0.2	5.0	50	6.2	8.1
1,1,2,2-Tetrachloroethane	1	0.2	5.6	50	8.2	6.1
1,2,3-Trichloropropane	1	0.4	2.4	50	16.5	3.0
n-Propylbenzene	1	0.1	12.1	50	3.4	14.8
Bromobenzene	1	0.1	13.2	50	7.8	6.4
1,3,5-Trimethylbenzene	1	0.1	8.1	50	4.0	12.4
tert-Butylbenzene	1	0.1	17.4	50	5.7	8.7
1,2,4-Trimethylbenzene	1	0.1	9.8	50	4.0	12.5
sec-Butylbenzene	1	0.1	9.7	50	7.6	6.6
p-Isopropyltoluene	1	0.1	9.5	50	5.4	9.3
1,3-Dichlorobenzene	1	0.1	7.2	50	7.3	6.8
1,4-Dichlorobenzene	1	0.1	7.7	50	6.1	8.2
1,2-Dichlorobenzene	1	0.1	6.9	50	7.7	6.5
1,2,3-Trimethylbenzene	1	0.1	7.6	50	5.7	8.7
n-Butylbenzene	1	0.1	11.1	50	4.8	10.3
Hexachloroethane	1	0.1	10.0	50	4.9	10.3
1,2-Dibromo-3-Chloropropan	1	0.1	7.6	50	27.6	1.8
1,2,4-Trichlorobenzene	1	0.2	5.0	50	8.0	6.2
Hexachlorobutadiene	1	0.2	6.2	50	10.3	4.8
1,2,3-Trichlorobenzene	1	0.1	8.5	50	7.6	6.6
Naphthalene	1	0.1	10.4	50	8.4	6.0
2-Methylnaphthalene	1	0.3	3.4	50	14.8	3.4

†: Data are from 03/04/06 (water) and 03/03/06 (soil).

Table 2b. Practical Quantitation Limits for Gasoline Range Organics[†]

COMPOUND	PQL _w (mg/L)	PQL _s (mg/kg)	MDL _w (mg/L)	MDL _s (mg/kg)	PQL _w /MDL _w	PQL _s /MDL _s
Gasoline Range Organics	0.2	5	0.0207	0.899	9.7	5.6

†: Data are from 07/13/2006.

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Table 3. Summary of Applicable Performance Compounds - Volatile Organics Analysis

# [†]	COMPOUND	CCC	SPCC	ISD	SSD	MS
1	PENTAFLUOROBENZENE			✓		
2	1,2-DICHLOROETHANE-D4				✓	
11	Chloromethane (SPCC)		✓			
12	Vinyl Chloride (CCC)	✓				
16	1,1-Dichloroethene (CCC/MS)	✓				✓
19	1,1-Dichloroethane (SPCC)		✓			
21	Chloroform (CCC)	✓				
25	1,4-DIFLUOROBENZENE			✓		
26	TOLUENE-D8				✓	
30	Benzene (MS)					✓
32	Trichloroethene (MS)					✓
33	1,2-Dichloropropane (CCC)	✓				
37	Toluene (CCC/MS)	✓				✓
42	CHLOROBENZENE-D5			✓		
43	4-BROMOFLUOROBENZENE				✓	
47	Chlorobenzene (SPCC/MS)		✓			✓
49	Ethylbenzene (CCC)	✓				
54	Bromoform (SPCC)		✓			
55	1,1,2,2-Tetrachloroethane (SPCC)		✓			
62	1,4-DICHLOROBENZENE-D4			✓		

[†]: Compound identification numbers listed are from calibration FR010910.M.

Key

CCC: Calibration Check Compound
 SPCC: System Performance Check Compound
 ISD: Internal Standard Compound
 SSD: Surrogate Standard Compound
 MS: Matrix Spiking Compound

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Table 4. GC/MS Operating Conditions - Volatile Organics Analysis

Operating Parameter	Volatiles Analysis
Chromatographic Column	DB 624, $L = 20\text{ m}$, $ID = 0.18\text{ mm}$
Carrier Gas	Helium (He)
Temperature Program	$T_0 = 30^\circ\text{C}$, hold 2.0 min $dT/dt_1 = 32^\circ\text{C/min}$ $T_1 = 195^\circ\text{C}$ $dT/dt_2 = 30^\circ\text{C/min}$ $T_2 = 235^\circ\text{C}$
Injector Temperature	250°C
Detector Temperature	280°C
Purge Volume	5 mL
Mass Scanning Range	$35\text{ m/z} - 250\text{ m/z}$
Mass Scanning Rate	2.0 Hz

Note: the above is subject to change based on GC and/or sample conditions.

Table 5. BFB Tune Evaluation Criteria

Target m/z	Relative m/z	LCL (%)	UCL (%)
50	95	8	40
75	95	30	66
95	95	100	100
96	95	5.0	9.0
173	174	0	2.0
174	95	50	120
175	174	4.0	9.0
176	174	93	101
177	176	5.0	9.0

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Table 6. Commonly Used Dilutions for Sample Preparation

Dilution	Sample Volume (μL)	H₂O Volume (μL)	ISD/SSD Volume (μL)	Total Volume (μL)
1:1	5000	0	10.0	5010
2:1	2500	2500	10.0	5010
5:1	1000	4000	10.0	5010
10:1	500	4500	10.0	5010
20:1	250	4750	10.0	5010
50:1	100	4900	10.0	5010
100:1	50	4950	10.0	5010
200:1	25	4975	10.0	5010
500:1	10	5000	10.0	5020
1000:1	5.0	5000	10.0	5015
2500:1	2.0	5000	10.0	5012

General "*n*:1" dilution: (5000/*n*) μ L of Sample
 (5000 - 5000/*n*) μ L H₂O
 10 μ L Internal/Surrogate Standard (ISD/SSD) at 25 mg/L

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Table 7. Quality Control Items, Frequency, and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Prior to all analytical runs	Method-based	Examine the entire analytical system; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate.
BFB	12-hour	Method-based	Re-attempt injection; clean MS source, re-tune; failure requires the re-analysis of all associated analytical runs.
SPCC/CCC	12-hour	Method-based	Re-attempt injection; some or all of the following: clean MS source, re-tune, clip/replace column, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Lab-based	A failed LCS should be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS should be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	n/a	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	n/a	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated analytical system (typically the purge-and-trap system) should result in a thorough cleansing of the affected system and sample/blank re-analysis.
Internal Standard	All samples	Method-based	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract or re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged appropriately. A negative bias unrelated to matrix effects indicates the need to: clean the MS source, re-tune, and re-calibrate
Surrogate Standard	All samples	Lab-based	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract or re-analyzing the sample within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample should be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

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Table 8. Summary of Control Limits: Surrogate and Matrix Spiking Compounds Percent Recovery[†]

# [‡]	COMPOUND	Water Matrix		Solid Matrix	
		LCL (%)	UCL (%)	LCL (%)	UCL (%)
2	1,2-DICHLOROETHANE-D4	66.4	124.8	70.0	136.3
26	TOLUENE-D8	82.5	118.4	84.0	138.0
43	4-BROMOFLUOROBENZENE	78.4	119.6	59.0	122.8
16	1,1-Dichloroethene (CCC/MS)	59.9	145.0	59.0	172.0
30	Benzene (MS)	73.7	127.0	66.0	142.0
32	Trichloroethene (MS)	71.0	121.2	62.0	137.0
37	Toluene (CCC/MS)	71.4	127.6	59.0	139.0
47	Chlorobenzene (SPCC/MS)	75.0	130.0	60.0	133.0
n/a	Gasoline Range Organics	70.0	130.0	70.0	130.0

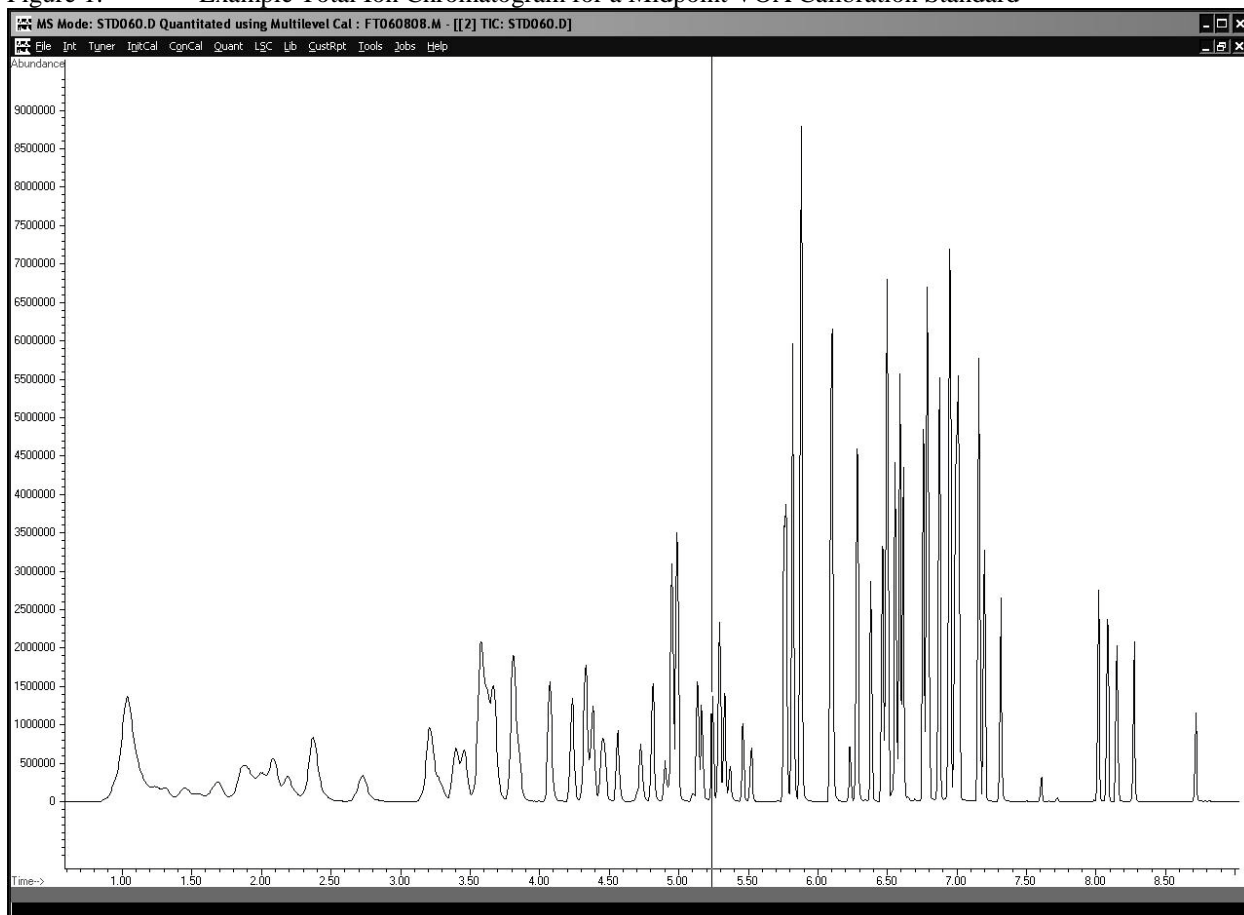
[†]: Results based on recovery data from 2001.

[‡]: Compound identification numbers listed are from calibration FR010910.M.

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Figure 1. Example Total Ion Chromatogram for a Midpoint VOA Calibration Standard[†]

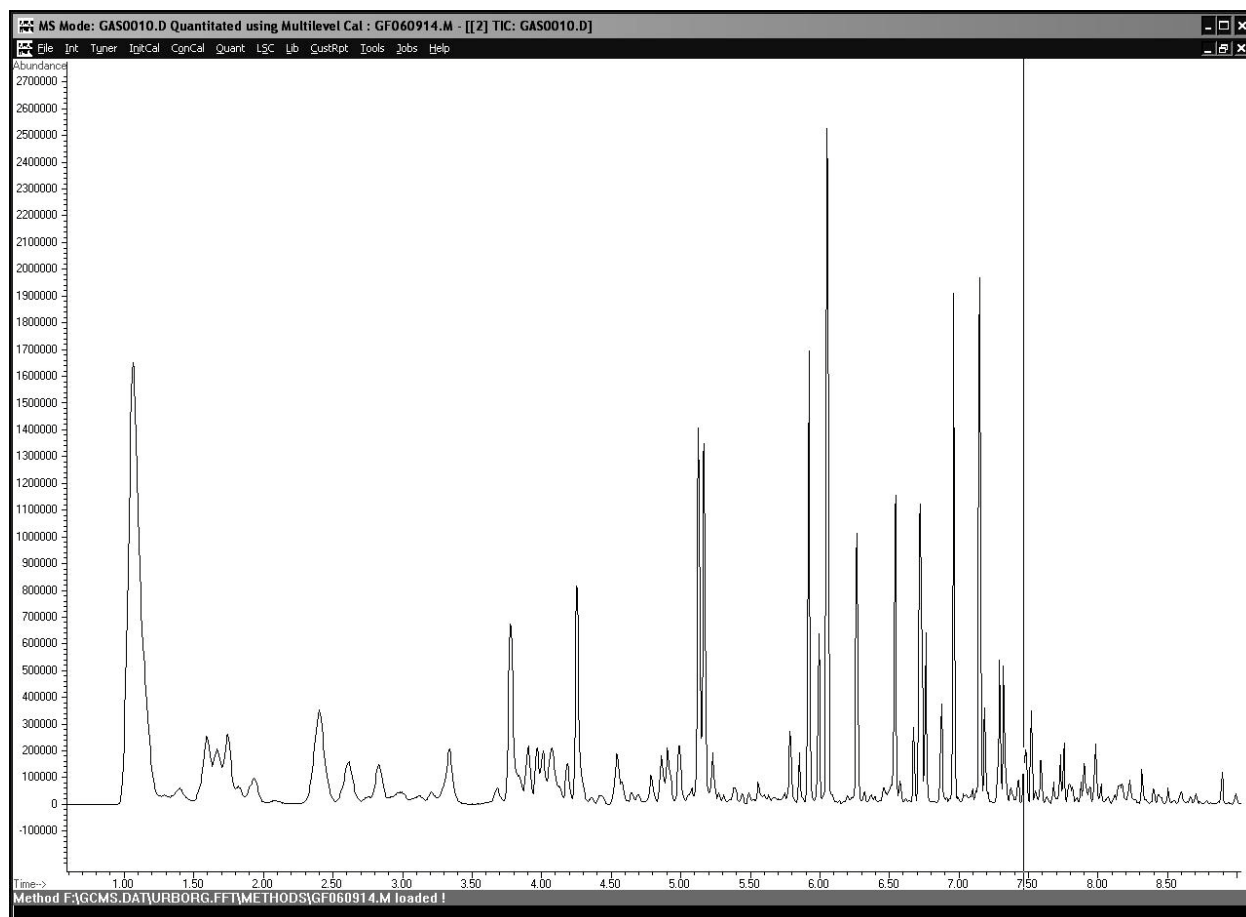


[†]: Data file Std060.D (60 µg/L). GC/MS acquisition parameters are given by Table 4.

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Figure 2. Example Total Ion Chromatogram for a Gasoline Range Organics Calibration Standard[†]



[†]: Data file GAS_010.D from calibration GF060914.M (1.0 mg/L). GC/MS acquisition parameters are given by Table 4.

METHOD 5030B/5035

1. SCOPE AND APPLICATION

- 1.1. This Sop describes a purge-and-trap procedure for the analysis of volatile organic compounds (VOCs) in aqueous samples and water miscible liquid samples. It also describes the analysis of low and high concentration soil and waste sample extracts prepared in Method 5035. The method is applicable to GC/MS Method 8260.
- 1.2. Method 5030 can be used for most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax or a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.
- 1.3. Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system or by dilution of the sample prior to the purge-and-trap process.
- 1.4. This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.
- 1.5. This SOP is not for use with samples that come into the lab for OHIO VAP work.

2. SUMMARY OF METHOD

- 2.1. Aqueous Samples: An inert gas is bubbled through a portion of the aqueous sample at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.
- 2.2. High Concentration Extracts from Method 5035: An aliquot of the extract prepared in Method 5035 is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and-trap GC or GC/MS following the normal aqueous method.
- 2.3. Low Concentration Soils: An aliquot of the soil is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and-trap GC or GC/MS.
- 2.4. Air samples in Tedlar Bags: A volume of air is extracted from the Tedlar Bag using a gas tight syringe and is introduced to a vial of reagent water. An inert gas is bubbled through a portion of the aqueous sample at ambient temperature. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

3. INTERFERENCES

- 3.1. Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealant, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.
- 3.2. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.
- 3.3. Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the entire system may be required.
- 3.4. The laboratory where volatiles analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage areas should be isolated from all atmospheric sources of methylene chloride. Otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4. APPARATUS AND MATERIALS

- 4.1. Microsyringes - 10- μ L, 25- μ L, 100- μ L, 250- μ L, and 500- μ L
- 4.2. Gas tight 5ml syringes.
- 4.3. Vials – 40-mL, for GC autosampler (Archon).
- 4.4. Magnetic stir bars.
- 4.5. Scale capable of displaying weight to the nearest hundredth of a gram.
- 4.6. Purge-and-trap device (Tekmar 3000). The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber.
 - 4.6.1. The Vocab3000 trap by Supelco is used. It is preconditioned at 270°C for 60 minutes upon installment as suggested by supplier.
- 4.7. Gas Chromatograph (HP5890).

5. REAGENTS

- 5.1. Organic-free reagent water - All references to water in this method refer to organic-free reagent water.
- 5.2. Purge and Trap grade methanol.
- 5.3. Sodium Bisulfate
- 5.4. See method 8260B SOP for specifications on internal and surrogate standards.
6. SAMPLE COLLECTION, PRESERVATION, AND HANDLING
 - 6.1. Aqueous Samples
 - 6.1.1. Samples should be stored in capped bottles, with minimum headspace, at $(4 \pm 4)^{\circ}\text{C}$ in an area free of solvent fumes.
 - 6.1.2. All samples should be analyzed within 14 days of collection. Samples not analyzed within this period must be noted and data are considered minimum values. The pH of the samples is checked with pH strips after the sample has been prepared for the autosampler. If the pH is greater than 2 as determined by the pH strip the fact is noted. If the sample with $\text{pH} > 2$ is not analyzed within seven days of the collection date then it is noted on the report that the sample was not properly preserved.
 - 6.2. Soil Samples
 - 6.2.1. High concentration soil samples collected and preserved in the field. The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030B SOP.
 - 6.2.1.1. Add 10 mL of methanol to each vial. Seal the vial with the screw-cap and septum seal. Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible). Weigh the prepared vial to the nearest 0.01g, record the tare weight, and write it on the label.
 - 6.2.1.2. $(10 \pm 0.5)\text{g}$ of sample are weighed out and added to the vial in the field.
 - 6.2.1.3. Upon arrival to the lab, samples are stored at $(4 \pm 2)^{\circ}\text{C}$.
 - 6.2.2. High concentration soil samples collected without a preservative.
 - 6.2.2.1. When high concentration soil samples are collected without the use of a preservative, an EnCore sample container/sampler is employed.
 - 6.2.2.1.1. The EnCore sampler has not been thoroughly evaluated by the EPA as a sample storage device. Preliminary results indicate that storage in the EnCore device may be appropriate for up to 48 hours, and so samples collected this way should be preserved in methanol within 48 hours of the sampling date. This preservation is documented in the Methanol Prep. Log.
 - 6.2.2.2. Weigh out $(10 \pm 0.5)\text{g}$ of soil sample into a 40-mL vial and add 10-mL of Methanol.
 - 6.2.2.3. Sonicate for twenty minutes.

- 6.2.2.4. Sample extracts are transferred to 4 ml vials and stored at $(4 \pm 2)^{\circ}\text{C}$.
- 6.2.2.5. Frozen samples are not acceptable for all OHIO VAP samples.
- 6.2.3. Low concentration soil samples collected and preserved in the field. The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be preserved in the field with sodium bisulfate and reagent water and analyzed by the aqueous purge-and-trap equipment described in Method 5030B SOP. Note: The sampling and preservation techniques required for low concentration analysis vary widely by state and regulating agency. The end-use of the data should be considered before selecting a sampling and preservation technique and may include procedures not in Method 5035 SOP.
- 6.2.3.1. Add 5 mL of reagent water and a magnetic stir bar to each vial as well as 0.2g of sodium bisulfate for every 1g of sample to be collected. Seal the vial with the screw-cap and septum seal. Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible). Weigh the prepared vial to the nearest 0.01g, record the tare weight, and write it on the label.
- 6.2.3.2. $(1-5 \pm 0.5)\text{g}$ of sample are weighed out and added to the vial in the field.
- 6.2.3.3. Upon arrival to the lab, samples are stored at $(4 \pm 2)^{\circ}\text{C}$.
- 6.2.4. Low concentration soil samples collected without a preservative.
- 6.2.4.1. When low concentration soil samples are collected without the use of a preservative, an EnCore sample container/sampler is employed.
- 6.2.4.1.1. The EnCore sampler has not been thoroughly evaluated by the EPA as a sample storage device. Preliminary results indicate that storage in the EnCore device may be appropriate for up to 48 hours, and so samples collected this way should be preserved with sodium bisulfate within 48 hours of the sampling date. This preservation is documented in the Prep. Log.
- 6.2.4.2. Weigh out $(1-5 \pm 0.5)\text{g}$ of soil sample into a 40-mL vial and add 5ml of reagent water and 0.2g of sodium bisulfate for every 1g of sample.
- 6.2.4.3. The preserved samples are stored at $(4 \pm 2)^{\circ}\text{C}$.

7. PROCEDURE

- 7.1. The purge-and-trap technique for aqueous samples is found in Sec. 7.2 and method for analysis of solvent extracts from the High Concentration Method in Method 5035 is found in Sec. 7.3. The gas chromatographic determinative steps are found in Methods 8260B SOP. The method is also applicable to the analysis of gasoline, using Method 8015M SOP.
- 7.2. This section provides guidance on the analysis of aqueous samples and samples that are water miscible, by purge-and-trap analysis.
- 7.2.1. Initial calibration.

7.2.2. Prior to using this introduction technique for any GC method, the system must be calibrated. General calibration procedures are discussed in Method 8260B SOP.

7.2.3. Sample screening

7.2.3.1. Screening of the sample prior to purge-and-trap analysis may provide guidance on whether sample dilution is necessary and may prevent contamination of the purge-and-trap system.

7.2.4. Sample introduction and purging

7.2.4.1. Assemble the purge-and-trap device. The operating conditions for the GC and GC/MS are given in method 8260B SOP.

7.2.4.2. GC or GC/MS calibration verification criteria must be met (Method 8260B SOP) before analyzing samples.

7.2.4.3. Adjust the purge gas flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response.

7.2.4.4. Use a 5-mL syringe to take a 5-mL aliquot of the sample. Care must be taken to remove any bubbles from the syringe. This process of taking an aliquot destroys the validity of the liquid sample for future analysis. Re-analysis should be done with duplicate VOA.

7.2.4.5. Add 10.0 μ L of surrogate and internal spiking solution as well as any matrix spike if applicable as described in method 8260B SOP.

7.2.4.6. Inject the aliquot into a 40-mL VOA and immediately place cap with septum and tighten.

7.2.4.7. Purge for 11.0 minutes at room temperature in the 40ml vial.

7.2.5. Sample desorption

7.2.5.1. Non-cryogenic interface - After the recommended purge (see above), place the purge-and-trap system in the desorb mode and preheat the trap without a flow of carrier gas passing through the trap. Start the flow of the carrier gas, begin the GC temperature program, and start GC data acquisition.

7.2.6. Trap Reconditioning

7.2.6.1. After desorbing the sample, recondition the trap by baking it.

7.3. This section provides guidance on the analysis of solvent extracts from High Concentration Samples prepared by Method 5035.

7.3.1. The GC or GC/MS system should be set up as in specific determinative method (8260B SOP).

7.3.2. Take 5mL's of organic-free reagent water and add 10.0 μ L of surrogate and internal spiking solution as well as any matrix spike if applicable as described in method 8260B SOP.

7.3.3. Measure out a 100 μ L aliquot of the methanol phase of the sample.

7.3.4. Quickly inject the 5-mL reagent water with standard mixture and 100µL of sample into a 40-mL vial and place cap with septum on it and tighten.

7.3.5. Purge for 11.0 minutes at room temperature in the 40ml vial.

7.3.6. Desorb the sample and recondition the trap (see 7.2.5 and 7.2.6).

7.4. This section provides guidance on the analysis of Low Concentration Samples prepared by Method 5035.

7.4.1. The GC or GC/MS system should be set up as in specific determinative method (8260B SOP).

7.4.2. Internal standards, surrogates and matrix spikes (if applicable) should be added automatically by the autosampler or manually by puncturing the septum using a small gauge needle.

7.4.3. Prior to purging the sample is preheated to 40°C for 1.0 minute while being agitated by the magnetic stir bar.

7.4.4. Purge for 11.0 minutes at 40°C while being agitated by the magnetic stir bar in the 40ml vial.

7.4.5. Desorb the sample and recondition the trap (see 7.2.5 and 7.2.6).

7.5. Tedlar Bag Air Analysis

7.5.1. The GC or GC/MS system should be set up as in specific determinative method (8260B SOP).

7.5.2. To a 40 ml VOA bottle add 5 ml reagent water and add 10.0 µL of surrogate and internal spiking solution as well as any matrix spike if applicable as described in method 8260B SOP.

7.5.3. Take a gas tight syringe with a needle fixed to the tip. Draw in a small volume of DI water into the syringe. This will provide a bubbling effect to show air is being drawn in from the bag.

7.5.4. Insert the needle of the syringe through the septa of the Tedlar Bag and with draw 5 cc into the syringe.

7.5.5. Bubble into 40 ml VOA bottle with 5 ml of DI water and surrogates and internal standards then cap promptly.

7.5.6. Purge for 11.0 minutes at room temperature in the 40ml vial.

7.5.7. Desorb the sample and recondition the trap (see 7.2.5 and 7.2.6).

7.6. Sample analysis. The samples prepared by this method will be analyzed according to method 8260B SOP.

8. QUALITY CONTROL

8.1. Refer to method 8260B SOP for specific quality control procedures.

9. METHOD PERFORMANCE

10. Refer to the determinative methods for performance data.

11.0 APPROVAL AND ISSUE

- 11.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

12.0 SAFETY

- 12.1 Eye protection and gloves must be worn while performing Volatile analyses.
- 12.2 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 12.3 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
- 12.4 A reference file of material safety data sheets (MSDSs) is available to all personnel.
- 12.5 Specific attention be paid (but not limited) to
- 12.5.1 Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.
- 12.5.2 Methanol may react violently with acids, acid chlorides, acid anhydrides, oxidizing agents, reducing agents and alkali metals. Protect from moisture. Highly flammable.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

- 13.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.
- 13.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.0 APPROVAL & ISSUE:

- 14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

Analyst	Date
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QA Officer	Date
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Maya V. Murshak, Technical Director	Date
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15.0 REFERENCES

- 15.1 U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.
- 15.2 Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November, 1991.

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METHOD 8270C/8015M (DRO)

1.0 SCOPE AND APPLICATION

- 1.1 This method can be used to quantitate most basic, neutral and acidic organic compounds (BNAs) that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons (PNAs), chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Tables 1a and 1b for a list of compounds (along with their characteristic ions) that have been evaluated.
- 1.2 In most cases, this method is not appropriate for the quantitation of multicomponent analytes, e.g., Aroclors, Toxaphene, Chlordane, *etc.*, because of limited sensitivity for those analytes. When these analytes have been identified by another technique, this method is appropriate for confirmation of the presence of these analytes when concentration in the extract permits. However, this method is used for the analysis of petroleum hydrocarbons, namely diesel range organics (DROs). DROs correspond to the range of alkanes from C₁₀ to C₂₈ and covering a boiling point range of approximately 170°C - 430°C. The identification of specific fuel types may be complicated by environmental processes such as evaporation, biodegradation, or when more than one fuel type is present.
- 1.3 The following compounds may require special treatment when being determined by this method:
- Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.
 - Under the alkaline conditions of the extraction step from aqueous matrices, α -BHC, β -BHC, Endosulfan I and II, and Endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected.
 - Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
 - N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.
 - N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.
 - Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.
 - Pyridine may perform poorly at the GC injection port temperatures listed in the method. Lowering the injection port temperature may reduce the amount of degradation. The analyst needs to use caution if modifying the injection port temperature as the performance of other analytes may be adversely affected.
 - In addition, analytes in the list provided above are flagged when there are limitations caused by sample preparation and/or chromatographic problems.
- 1.4 The estimated quantitation limit (PQL) of Method 8270/8015 for determining an individual compound is approximately 330 µg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for ground water samples (see Tables 2a and 2b). For DROs, the values are 4 mg/kg (soil/sediment, wet weight) and 0.1 mg/L for ground water (see Table 2c). PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

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- 1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

- 2.1 The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) using the appropriate sample preparation (refer to Methods 3500, 3510, 3550).
- 2.2 The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.
- 2.3 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point (or more) calibration curve.
- 2.4 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

- 3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.
- 3.2 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. This is virtually never a problem for direct injection GC/MS analysis, provided that the sample syringe is rinsed with solvent between sample injections. If carryover is suspected, questionable samples should be re-injected after the system has been demonstrated to be free of contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph/mass spectrometer system

- 4.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.
- 4.1.2 Column - 30 m \times 0.25 mm ID \times 0.5 μ m film thickness silicone-coated fused-silica capillary column (Hewlett Packard HP-5ms SV or equivalent).
- 4.1.3 Mass spectrometer capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 4 when 1 μ L of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP)
- 4.1.4 GC/MS interface - Any GC-to-MS interface may be used that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria. For a narrow-bore capillary column, the interface is usually capillary-direct into the mass spectrometer source.
- 4.1.5 Data system - A computer system is interfaced to the mass spectrometer. Hewlett-Packard Chemstation software (with environmental data analysis) is used to acquire and process GC/MS data.

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- 4.2 Syringes - 1 to 1000 μ L Hamilton syringes are used in the preparation of standards, spiking solutions, and standards.
- 4.3 Balance - Analytical, capable of weighing 0.0001 g.
- 4.4 Bottles - glass with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

5.0 REAGENTS

- 5.1 Reagent grade inorganic chemicals shall be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without introducing adverse interferences.
- 5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water.
- 5.3 Stock standard solutions
 - 5.3.1 Certified stock standard solutions are purchased when available for the bulk of desired analytes. They are typically available at concentrations of 1000 to 2000 mg/L.
 - 5.3.2 Supplemental compounds added to calibration mixes are generally prepared gravimetrically from neat standard references (in order to create a stock solution of 1000 to 10000 mg/L).
 - 5.3.3 Stock standard solutions are stored in bottles with PTFE-lined screw-caps. They are refrigerated and protected from light, as recommended by the standard manufacturer.
 - 5.3.4 Neat standard references are used in order to create a stock solution ~10000 mg/L for DRO standards.
 - 5.3.5 Stock standard solutions are replaced prior to expiration, or sooner if comparison with quality control check samples indicates a problem.
- 5.4 Internal standard solutions - The internal standards used are 1,4-Dichlorobenzene- d_4 , Naphthalene- d_8 , Acenaphthene- d_{10} , Phenanthrene- d_{10} , Chrysene- d_{12} , and Perylene- d_{12} . Internal standards are spiked into the sample extracts and calibration standards at a uniform concentration of 40 ng/ μ L (\equiv 40 mg/L).
- 5.5 GC/MS tuning standard - A methylene chloride solution containing 50 ng/ μ L of decafluorotriphenylphosphine (DFTPP), pentachlorophenol, and benzidine is used to evaluate GC/MS tuning criteria, injection port inertness, and GC column performance.
- 5.6 Calibration standards - A minimum of five calibration standards should be prepared at five different concentrations. If possible, the lowest calibration standard corresponds to a sample concentration at or below the standard reporting limit. The remaining standards should correspond to the working range of the GC/MS system (10-100 ng/ μ L for BNAs, 2-100 ng/ μ L for PNAs, and 0.1-1.0 g/L for DROs). Each standard should contain each analyte for detection by this method. The preparation instructions for the creation of calibrations standards from stock solutions commonly used in BNA, PNA, and DRO analysis are found in the Calibration Recipes excel file.
- 5.7 Surrogate standards - The surrogates used are Phenol- d_6 , 2-Fluorophenol, 2,4,6-Tribromophenol, Nitrobenzene- d_5 , 2-Fluorobiphenyl, and p-Terphenyl- d_{14} . See Method 3500 for instructions on preparing the surrogate solutions. For BNA analysis, all six surrogate standards are used. For PNA analysis, only Nitrobenzene- d_5 , 2-Fluorobiphenyl, and p-Terphenyl- d_{14} are used.
 - 5.7.1 Surrogate spiking mixes are created at 100 mg/L and spiked into samples in 1 mL aliquots. The resulting ideal concentration in a 1 mL extract as 100ng/ μ L.
 - 5.7.2 Surrogate Standard Check: inject a sample of the spiking solution (with internal standard added) into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.

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- 5.8 Matrix spike and laboratory control standards - See Method 3500 for instructions on preparing the matrix spike standard. The same standard is used as the laboratory control standard (LCS).
 - 5.8.1 Matrix spiking mixes for single component analytes are generally created at 50 mg/L and spiked into samples in 1 mL aliquots. The resulting ideal concentration in a 1 mL extract is 50ng/μL.
 - 5.8.2 The matrix spiking mix for DRO is created at 1000 mg/L and spiked into samples in 1 mL aliquots. The resulting ideal concentration in a 1 mL extract is 1000 ng/μL.
 - 5.8.3 Matrix Spike Check: inject a sample of the spiking solution (with internal standard added) into the GC/MS to determine recovery of surrogate standards. It is recommended that this check be done whenever a new surrogate spiking solution is prepared.
 - 5.9 Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene, and other appropriate solvents - All solvents should be pesticide quality or equivalent.
- 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING
- 6.1 Unanalyzed sample extracts are refrigerated and protected from light in sealed vials.
 - 6.2 The holding time for samples is 7 days until extraction and 40 days thereafter.
 - 6.3 Samples and target compound standards are stored separately.
- 7.0 PROCEDURE
- 7.1 Sample preparation
 - 7.1.1 Soil and water are normally prepared via an extraction procedure (*cf.* Methods 3500, 3510, 3550; SOPs: 3510bna.doc and 3550bna.doc) prior to GC/MS analysis.
 - 7.1.2 In cases where the sample is an oil or a solvent, the sample is simply diluted with methylene chloride and analyzed at a concentration appropriate for the level of analytes/interferences in the sample. In this situation, the sample is reported on a weight basis and analyzed in a batch of soil samples.
 - 7.2 GC/MS operating conditions - see Table 3 for routine operating conditions for both BNA and PNA analysis.
 - 7.3 Initial calibration
 - 7.3.1 The GC/MS system must be hardware-tuned using a 50 ng injection of DFTPP prior to the analysis of calibration standards and samples.
 - 7.3.1.1 In the absence of any other manipulations, evaluate the mass spectrum of the highest intensity level from the total ion chromatogram for the DFTPP peak. This is the default approach used.
 - 7.3.1.2 If the above evaluation is adversely affected by ion peak asymmetry, average the three highest intensity scans of the peak or average the mass spectrum ranging from the 10% initial peak intensity to the tailing 10% peak intensity level from the total ion chromatogram for the DFTPP peak.
 - 7.3.1.3 If the above evaluation is adversely affected by background contamination, perform a background subtraction with a spectrum within 20 scans of the DFTPP peak which does not represent a target compound. Use of this procedure may be indicative of failing MS performance. The MS source should be cleaned and re-tuned.
 - 7.3.1.4 The DFTPP mass intensity criteria in Table 4 are used as tuning acceptance criteria.

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- 7.3.1.5 All subsequent standards, samples, MS/MSDs, and blanks associated with a DFTPP analysis must use the identical mass spectrometer instrument conditions.
- 7.3.1.6 The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Benzidine and pentachlorophenol should be present at their normal responses, and peak tailing should be minimal.
- 7.3.1.7 The injection port is replaced prior to any calibration sequence or 12-hour BNA analytical sequence. If chromatography is still poor, it may also be necessary to clip off the first 6-12 in. of the capillary column. Clipping the column may necessitate recalibration, as retention times and responses can shift considerably.
- 7.3.2 Analyze 1-2 μL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each target analyte (as indicated in Tables 1a and 1b). A set of at least five calibration standards is necessary. The injection volume must be the same for all standards and sample extracts. Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes. Depending on the current state of the GC/MS system, a 2 μL injection may be required to achieve appropriate responses for the lower levels of the least sensitive compounds. When possible, however, a 1 μL can be used to yield a better dynamic range for the high sensitivity compounds.
- 7.3.3 Calculate response factors (RF s) for each target analyte relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the areas of the standard compound and corresponding internal standard, respectively. Likewise, C_s and C_i are the respective concentrations (in any consistent set of units) of the standard compound and corresponding internal standard.
- 7.3.4 System performance check compounds (SPCCs)
 - 7.3.4.1 A system performance check must be performed to ensure that minimum RF s are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol.
 - 7.3.4.2 The minimum acceptable average RF for these compounds is 0.050. These SPCCs typically have low RF s (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.
 - 7.3.4.3 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. Replacing the calibration standards, and/or clipping/replacing the column will likely solve this problem.
- 7.3.5 Calibration check compounds (CCCs)
 - 7.3.5.1 The purpose of the CCCs is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is in addition to the successful calibration of the target analytes using one of the approaches described in Section 7.0 of Method 8000.
 - 7.3.5.2 Calculate the mean response factor and the relative standard deviation (RSD) of the response factors for each target analyte. The RSD should be less than or equal to 15%

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for each target analyte. However, the RSD for each individual CCC (see Semi Volatile QC Reference) must be less than or equal to 30%.

- 7.3.5.3 If the RSD of any CCC is greater than 30%, then the chromatographic system is too reactive for analysis to begin. Clean or replace the injector liner and/or capillary column, then repeat the calibration procedure.
- 7.3.6 Evaluation of retention times - The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. This is accomplished by setting the retention time extraction windows in the Chemstation software.
- 7.3.7 Linearity of target analytes - If the %RSD of any target analytes is 15% or less, then the relative response factor may be assumed to be constant over the calibration range, and the average relative response factor may be used for quantitation
 - 7.3.7.1 Refer to Method 8000 if a least-squares regression is used to determine a linear or quadratic fit to the calibration data. Note that quadratic polynomials are generally fit through the origin in order to prevent the symptomatic aphysical prediction of high concentrations at very low responses. (All least-squares regressions used for OHIO VAP analysis will use a calculated intercept and quadratic fits will only be used for compounds exhibiting nonlinear behavior). In any event, the COD for any regression fit should be ≥ 0.99 . In addition, 6 calibration data points are required for a calibration fit with 3 free parameters, while 5 are required for a calibration fit with 1 or 2 free parameters.
 - 7.3.7.2 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, *etc.*
 - 7.3.7.3 The quality of the calibration fit for any particular compound is communicated to the data user via the Quality Control report for a given batch of samples. The calibration summary report includes: the concentration and RF for each standard in the calibration curve, the type of calibration fit, the calibration fit parameters (*i.e.* average RF or regression coefficients), and the appropriate calibration quality metric (*i.e.* %RSD or COD).
- 7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.
 - 7.4.1 Prior to the analysis of samples or calibration standards, inject 50 ng of the DFTPP standard into the GC/MS system. The resultant mass spectrum for DFTPP must meet the criteria given in Table 4 before sample analysis begins. These must be *injected* within 12 hours of the injection time for the DFTPP.
 - 7.4.2 The initial calibration for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique and conditions used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration (50 ng/ μ L) for the calibration range of the GC/MS. The results from the calibration standard analysis must meet the verification acceptance criteria provided below for the SPCC and CCC compounds.
 - 7.4.3 A method blank is run every 20 samples to ensure that the total system (preparation glassware, introduction device, transfer lines, and the GC/MS system itself) is free of contaminants.
 - 7.4.4 System performance check compounds (SPCCs)

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- 7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC in the calibration verification standard must meet a minimum response factor of 0.050. This is the same check that is applied during the initial calibration.
- 7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins (see previous).
- 7.4.5 Calibration check compounds (CCCs)
- 7.4.5.1 After the system performance check is met, the CCCs listed in Semi Volatile Organic QC Reference are used to check the validity of the initial calibration. Percent drift is used to evaluate the CCC response and it must be $\leq 20\%$. Drift is defined as the normalized deviation of the measured from the spike value of a target component:
- $$\%D = \left| C - C_{\text{spike}} \right| / C_{\text{spike}} \cdot$$
- 7.4.5.2 If the percent drift for each CCC is $\leq 20\%$, then the initial calibration is assumed to be valid. If the criterion is not met for any one CCC, then corrective action must be taken prior to the analysis of samples (see previous).
- 7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins.
- 7.5 GC/MS analysis of samples
- 7.5.1 Samples are screened at a diluted state via GC/MS whenever possible prior to analysis within a 12-hour QC batch. This can identify potentially low surrogate recoveries, high target compound concentrations, non-target matrix interferences. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.
- 7.5.2 Allow the sample extract to warm to room temperature. 3 μL of the internal standard solution is added to a 300 μL aliquot of sample in a crimp-top vial for subsequent autosampler analysis. If the sample extract is to be diluted prior to analysis, a smaller sample volume is used (even though the net volume of nominally 300 μL remains the same). The Dilution Reference has a list of commonly used dilutions as well as the required amount of sample, solvent, and internal standard for each dilution.
- 7.5.3 Inject a 1-2 μL aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration.
- 7.5.4 If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system by more than 10%, the sample extract should be diluted and reanalyzed. In any event, a result based on an extrapolation of calibration curve beyond the working range is flagged on the analytical report.
- 7.5.5 The EICP area for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. Changes by more than a factor of two (*i.e.* 50% to 200%) can indicate adverse matrix effects (in the case of an isolated sample) or degrading MS performance (in the case of a systematic low bias). A single-sample matrix effect is documented either via screening or re-analysis and is noted on the analytical report (see Semi Volatile QC Reference). Similarly, the retention times for all of the internal standards in all spikes, blanks, and samples is monitored relative to the most recent calibration verification standard. The change in retention time for any internal standard by more than 30 seconds of the most recent calibration verification standard is indicative of the same potential problems listed above and should be flagged/corrected as appropriate.
- 7.6 Qualitative analysis

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- 7.6.1 The qualitative identification of compounds determined by this method is based on retention time and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are given in Tables 1a and 1b. Compounds are identified when the following criteria are met.
- 7.6.1.1 Initial selection of a target compound peak is performed by the Chemstation data system search routine. The search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time.
 - 7.6.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component. This is accomplished using retention time extraction windows within the Chemstation data system.
 - 7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)
 - 7.6.1.4 Structural isomers that produce very similar mass spectra are identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.
 - 7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (*i.e.*, a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.
 - 7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in qualitative identification of compounds. When analytes coelute (*i.e.*, only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.
 - 7.6.1.7 In the two previous cases, analyst expertise as well as knowledge of site history may be important in accepting/rejecting the identification of a compound. In the event of continued uncertainty, the analyst should preferentially make a conservative judgement and accept an identified hit, allowing the potential for a false positive.
- 7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Guidelines for tentative identification are:
- Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.
 - The relative intensities of the major ions should agree within $\pm 20\%$.
 - Molecular ions present in the reference spectrum should be present in the sample spectrum.

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- Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

- 7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance of the primary characteristic ion from the EICP.
- 7.7.2 The curve fit applied in the initial calibration is the same as that used to compute the concentration of a target analyte in a sample. All curve fits are evaluated by the data system and are of the form: $A_s/A_i = k_0 + k_1[C_s/C_i] + k_2[C_s/C_i]^2$. Here A_s and A_i are the areas of the target and internal standard, C_s and C_i are the concentrations of the target and internal standard, and k_i is the i^{th} -order regression coefficient. Note that for a mean RF fit to the calibration data, $k_1 \equiv \langle \text{RF} \rangle$, while k_0 , $k_2 \equiv 0$.
- 7.7.3 The concentration of any non-target analytes identified in the sample may be estimated by assuming a mean RF of 1 and by using the TIC areas for the nearest internal standard and target compound. The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.
- 7.7.4 Structural isomers that produce very similar mass spectra should be quantitated as individual isomers if they have sufficiently different GC retention times. Otherwise, structural isomers are quantitated as isomeric pairs (such as p- and m-cresol).
- 7.8 Special procedures for diesel range organics (DROs) - The following items detail the differences in the calibration procedures for multicomponent, diesel range organics from the general, single component procedures outlined above.
- 7.8.1 A set of at least five calibration standards per §7.2 and §7.3.2. The preparation instructions for the creation of the DRO calibration standards can be found in the Calibration Recipes excel file. Figure 2 represents a DRO chromatogram.
- 7.8.2 Instead of using the measured responses from the TIC to represent the DRO calibration, the total area of ions characteristic to the fuel in question is used in an internal standard calibration. Using characteristic ions to represent a fuel has the advantage of reducing biases from other components present in the chromatogram (namely surrogate and internal standards), and the use of an internal standard improves the stability of a calibration. Diesel range organics consist primarily of straight and branched alkanes ($\sim C_{10}$ to C_{28}). For the alkanes, the characteristic mass used is $m/z = 57$ (corresponding to the ion $C_4H_9^+$). This single ion is used for quantitation.
- 7.8.3 Calculate response factors (RFs) for each target mass relative to one of the internal standards as follows: $RF = A_s C_i / A_i C_s$. Here, A_s and A_i are the areas of the characteristic mass over its respective time range and corresponding internal standard, respectively. Likewise, C_s and C_i are the respective concentrations (in any consistent set of units) of the *total fuel* and corresponding internal standard. The characteristic time ranges for each mass depend upon current chromatographic conditions. The time ranges used for the sample chromatograms in Figures 1 and 2 are listed in the respective figure.
- 7.8.4 The relative area response vs. relative concentration for each characteristic mass is calibrated in the same manner as described in §7.3.7 and §7.7.
- 7.8.5 The net result for a DRO analysis is based upon the single characteristic mass (57).

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- 7.8.6 In addition the routine SPCC/CCC check standard, a DRO check standard is analyzed in order to characterize the efficacy of the present DRO calibration in terms of recovery and retention times.

8.0 QUALITY CONTROL

- 8.1 All of the quality control items employed and evaluated are listed in Semi Volatile QC Reference. In addition, the Semi Volatile QC Reference indicates the frequency of each QC item along with appropriate courses of corrective action.
- 8.2 Quality control items are inspected by the analyst as the data becomes available. At the conclusion of the analytical batch, all of the samples, spikes, standards, *etc.* are processed and evaluated automatically and stored electronically for future reference/retrieval.

9.0 METHOD PERFORMANCE

- 9.1 Laboratory-specific performance data is provided in this document
- 9.2 Tables 2a, 2b, and 2c present the results for the most recent detection limit studies. The MDL, PQL and ratio of PQL/MDL are given for each analyte in the BNA and PNA target compound lists.
- 9.3 Lower and upper acceptance limits for all surrogate and matrix spiking compounds can be found in the Semi Volatile QC Reference.

10.0 REFERENCES

1. SW-846, 1996, Revision 3; Methods 3500, 3510, 3550, 8000, 8015, 8270.

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11.0 APPROVAL AND ISSUE

_____ Analyst	_____ Date
_____ Andy Ball, QA Officer	_____ Date
_____ Maya V. Murshak, Technical Director	_____ Date

12.0 TABLES AND FIGURES

Table 1a. Summary of Retention Times[†] and Characteristic Ions for Base/Neutral/Acid Semi-Volatile Organics

Table 1b. Summary of Retention Times[†] and Characteristic Ions for Polynuclear Aromatic Semi-Volatile Organics

Table 2a. Summary of Practical Quantitation Limits for Base/Neutral/Acid Semi-Volatile Organics[†]

Table 2b. Summary of Practical Quantitation Limits for Polynuclear Aromatic Semi-Volatile Organics[†]

Table 2c. Practical Quantitation Limits for Diesel Range Organics

Table 3. GC/MS Operating Conditions - Base/Neutral/Acid (BNA) and Polynuclear Aromatic (PNA) Semi-Volatile Organics Analysis

Table 4. DFTPP Tune Evaluation Criteria

Figure 1. Example Total Ion Chromatogram for a Midpoint BNA Calibration Standard[†]

Figure 2. Example Total Ion Chromatogram for a Diesel Range Organics Calibration Standard[†]

Table 1a. Summary of Retention Times[†] and Characteristic Ions for Base/Neutral/Acid Semi-Volatile Organics

#	Compound	t _R (min)	t _R /t _{R,I} (-)	t _R -t _{R,I} (min)	1 ⁰ m/z	2 ⁰ m/z	3 ⁰ m/z	4 ⁰ m/z
1)	1,4-DICHLOROBENZENE-D4	6.92	1.000	0.00	152	150	115	
2)	N-Nitrosodimethylamine	3.79	0.548	-3.13	74	42	43	
3)	2-Picoline	4.61	0.666	-2.31	93	92	66	
4)	Methyl methanesulfonate	5.16	0.746	-1.76	80	79	95	
5)	2-Fluorophenol	5.31	0.767	-1.61	112	92	64	
6)	Ethyl methanesulfonate	5.99	0.866	-0.93	79	109	97	
7)	Phenol-d5	6.45	0.932	-0.47	99	71	42	
8)	Phenol **	6.47	0.935	-0.45	94	66	65	
9)	Aniline	6.53	0.944	-0.39	93	65	66	
10)	2-Chlorophenol **	6.68	0.965	-0.24	128	130	92	
11)	Bis(2-chloroethyl)ether	6.59	0.952	-0.33	93	63	95	
12)	1,3-Dichlorobenzene	6.94	1.003	0.02	146	148	111	
13)	1,4-Dichlorobenzene **	6.94	1.003	0.02	146	148	111	
14)	1,2-Dichlorobenzene	7.18	1.038	0.26	146	148	111	
15)	Bis(2-chloroisopropyl)ethe	7.3	1.055	0.38	45	121	77	
16)	Benzyl Alcohol	7.09	1.025	0.17	108	107	79	77
17)	Acetophenone	7.46	1.078	0.54	105	77	120	
18)	o-Cresol	7.24	1.046	0.32	108	107	79	
19)	p,m-Cresol	7.42	1.072	0.50	107	108	79	
20)	Hexachloroethane	7.59	1.097	0.67	117	119	201	
21)	N-Nitrosodi-n-propylamine*	7.48	1.081	0.56	70	43	42	41
22)	NAPHTHALENE-D8	8.59	1.000	0.00	136	68	108	
23)	Nitrobenzene-d5	7.66	0.892	-0.93	82	128	98	
24)	Nitrobenzene	7.69	0.895	-0.90	123	123	65	
25)	N-Nitrosopiperidine	7.89	0.919	-0.70	114	55	56	
26)	Isophorone	7.98	0.929	-0.61	82	95	138	
27)	2-Nitrophenol	8.11	0.944	-0.48	139	109	65	
28)	2,4-Dimethylphenol	8.12	0.945	-0.47	107	122	121	
29)	Bis(2-chloroethoxy)methane	8.25	0.960	-0.34	93	63	95	
30)	2,4-Dichlorophenol	8.4	0.978	-0.19	162	164	98	
31)	1,2,4-Trichlorobenzene **	8.52	0.992	-0.07	180	182	145	
32)	Naphthalene	8.61	1.002	0.02	128	127	129	
33)	4-Chloroaniline	8.69	1.012	0.10	127	129	65	
34)	2,6-Dichlorophenol	8.71	1.014	0.12	162	164	127	
35)	Hexachlorobutadiene	8.83	1.028	0.24	225	223	227	
36)	N-Nitroso-di-n-butylamine	9.13	1.063	0.54	84	116	158	
37)	4-Chloro-3-methylphenol **	9.28	1.080	0.69	107	142	77	
38)	2-Methylnaphthalene	9.5	1.106	0.91	141	142	115	
40)	1,2,4,5-Tetrachlorobenzene	9.77	1.137	1.18	216	214	218	
41)	Hexachlorocyclopentadiene	9.79	1.140	1.20	237	235	239	
42)	2,4,6-Trichlorophenol	9.94	1.157	1.35	196	198	200	
43)	2,4,5-Trichlorophenol	9.94	1.157	1.35	196	198	132	
44)	2-Fluorobiphenyl	9.98	1.162	1.39	172	171	173	
45)	2-Chloronaphthalene	10.13	1.179	1.54	162	127	164	
46)	1-Chloronaphthalene	10.18	1.185	1.59	162	164	127	
47)	2-Nitroaniline	10.29	1.198	1.70	138	65	92	

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#	Compound	t _R (min)	t _R /t _{R,I} (-)	t _R -t _{R,I} (min)	1 ⁰ m/z	2 ⁰ m/z	3 ⁰ m/z	4 ⁰ m/z
48)	Acenaphthylene	10.67	1.242	2.08	152	151	150	
49)	Dimethyl Phthalate	10.54	1.227	1.95	163	164	77	
50)	2,6-Dinitrotoluene	10.64	1.239	2.05	165	121	148	
51)	3-Nitroaniline	10.82	1.260	2.23	138	92	65	
52)	Acenaphthene **	10.91	1.270	2.32	154	153	152	
53)	2,4-Dinitrophenol	10.95	1.275	2.36	184	63	107	
54)	Dibenzofuran	11.12	1.295	2.53	168	169	139	
55)	4-Nitrophenol **	10.99	1.279	2.40	65	139	81	109
56)	2,4-Dinitrotoluene **	11.15	1.298	2.56	165	89	63	
57)	2,3,4,6-Tetrachlorophenol	11.32	1.318	2.73	232	230	234	131
58)	Fluorene	11.56	1.346	2.97	166	165	167	
59)	Diethyl phthalate	11.43	1.331	2.84	149	150	177	
60)	4-Chlorophenyl phenyl ethe	11.53	1.342	2.94	204	141	206	
61)	4-Nitroaniline	11.61	1.352	3.02	138	65	92	
62)	2,4,6-Tribromophenol	11.89	1.384	3.30	330	332	141	
63)	PHENANTHRENE-D10	12.8	1.000	0.00	188	80	94	
64)	4,6-Dinitro-2-methylphenol	11.67	0.912	-1.13	198	121	105	
65)	N-Nitrosodiphenylamine	11.69	0.913	-1.11	169	168	167	
66)	1,2-Diphenylhydrazine	11.74	0.917	-1.06	182	105	77	
67)	Azobenzene	11.74	0.917	-1.06	182	105	77	
68)	4-Bromophenyl phenyl ether	12.16	0.950	-0.64	248	250	77	
69)	1,3,5-Trinitrobenzene	12.08	0.944	-0.72	213	74	75	
70)	Phenacetin	12.11	0.946	-0.69	108	109	179	137
71)	Hexachlorobenzene	12.37	0.966	-0.43	249	282	286	
72)	4-Aminobiphenyl	12.51	0.977	-0.29	169	168	170	
73)	Pentachlorophenol **	12.6	0.984	-0.20	266	264	268	
75)	Pronamide	12.6	0.984	-0.20	173	174	145	
76)	Pentachloronitrobenzene	12.72	0.994	-0.08	237	249	295	
77)	Phenanthrene	12.83	1.002	0.03	178	176	179	
78)	Anthracene	12.83	1.002	0.03	178	176	179	
79)	di-N-butyl phthalate	13.62	1.064	0.82	149	150	104	
80)	Fluoranthene	14.65	1.145	1.85	202	200	203	
81)	Terphenyl-d14	15.28	1.194	2.48	244	122	212	
82)	CHRYSENE-D12	17.34	1.000	0.00	240	236	120	
83)	Benzidine	14.83	0.855	-2.51	184	185	92	
84)	Pyrene **	15.03	0.867	-2.31	202	200	203	
85)	p-Dimethylaminoazobenzene	15.57	0.898	-1.77	225	120	77	
86)	Butyl benzyl phthalate	16.23	0.936	-1.11	149	91	206	
88)	Benzo(a)anthracene	17.29	0.997	-0.05	228	226	229	
89)	3,3'-Dichlorobenzidine	17.25	0.995	-0.09	252	254	126	
90)	Chrysene	17.38	1.002	0.04	228	226	229	
92)	PERYLENE-D12	20.3	1.000	0.00	264	260	265	
91)	Bis(2-ethylhexyl)phthalate	17.42	0.858	-2.88	149	167	279	
93)	Di-n-octyl phthalate	18.66	0.919	-1.64	149	43	167	
95)	Benzo(b)fluoranthene	19.47	0.959	-0.83	252	253	126	
96)	7,12-Dimethylbenz(a)anthra	19.5	0.961	-0.80	256	241	239	
97)	Benzo(k)fluoranthene	19.47	0.959	-0.83	252	253	126	

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#	Compound	t_R (min)	$t_R/t_{R,I}$ (-)	$t_R - t_{R,I}$ (min)	$1^0 m/z$	$2^0 m/z$	$3^0 m/z$	$4^0 m/z$
98)	Benzo(a)pyrene	20.16	0.993	-0.14	252	253	126	
99)	3-Methylcholanthrene	21.04	1.036	0.74	268	252	253	269
100)	Dibenz(a,j)acridine	22.54	1.110	2.24	279	280	139	278
101)	Indeno(1,2,3-cd)pyrene	23.1	1.138	2.80	276	138	277	
102)	Dibenzo(a,h)anthracene	23.14	1.140	2.84	278	139	279	
103)	Benzo(ghi)perylene	23.92	1.178	3.62	276	138	277	

†: Absolute retention times (t_R) listed are from calibration BU061002.M. Absolute and relative retention times ($t_R/t_{R,I}$) may shift with the present condition of the column (*i.e.* new, clipped, *etc.*), but the differential retention times ($t_R - t_{R,I}$) tend to remain constant given the same chromatographic temperature program.

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Table 1b. Summary of Retention Times[†] and Characteristic Ions for Polynuclear Aromatic Semi-Volatile Organics

#	Compound	t_R (min)	$t_R/t_{R,I}$ (-)	$t_R - t_{R,I}$ (min)	$1^0 m/z$	$2^0 m/z$	$3^0 m/z$	$4^0 m/z$
1)	1,4-DICHLOROBENZENE-D4	3.96	1.000	0.00	152	152		
2)	NAPHTHALENE-D8	5.21	1.000	0.00	136	68	108	
3)	Nitrobenzene-d5	4.52	0.868	-0.69	82	54	128	
4)	Naphthalene	5.23	1.004	0.02	128	127	129	
5)	2-Methylnaphthalene	5.88	1.129	0.67	141	141	115	
6)	ACENAPHTHALENE-D10	6.94	1.000	0.00	164	162	160	
7)	2-Fluorobiphenyl	6.23	0.898	-0.71	172	171	173	
8)	Acenaphthylene	6.78	0.977	-0.16	152	151	150	
9)	Acenaphthene **	6.97	1.004	0.03	154	153	76	
10)	Fluorene	7.49	1.079	0.55	166	165	167	
11)	PHENANTHRENE-D10	8.52	1.000	0.00	188	80	94	
12)	Phenanthrene	8.54	1.002	0.02	178	176	179	
13)	Anthracene	8.6	1.009	0.08	178	176	179	
14)	Fluoranthene	10.09	1.184	1.57	202	200	203	
15)	Terphenyl-D14	10.62	1.246	2.10	244	122	212	
16)	CHRYSENE-D12	12.5	1.000	0.00	240	236	120	
17)	Pyrene **	10.44	0.835	-2.06	202	101	200	
18)	Benzo(a)anthracene	12.46	0.997	-0.04	228	226	229	
19)	Chrysene	12.54	1.003	0.04	228	226	229	
20)	PERYLENE-D12	15.22	1.000	0.00	264	260	132	
21)	Benzo(b)fluoranthene	14.51	0.953	-0.71	252	253	126	
22)	Benzo(k)fluoranthene	14.56	0.957	-0.66	252	253	125	
23)	Benzo(a)pyrene	15.12	0.993	-0.10	252	253	126	
24)	Indeno(1,2,3-cd)pyrene	17.38	1.142	2.16	276	138	277	
25)	Dibenzo(ah)anthracene	17.39	1.143	2.17	278	139	279	
26)	Benzo(ghi)perylene	17.99	1.182	2.77	276	138	277	

[†]: Absolute retention times (t_R) listed are from calibration PF060829.M. Absolute and relative retention times ($t_R/t_{R,I}$) may shift with the present condition of the column (*i.e.* new, clipped, *etc.*), but the differential retention times ($t_R - t_{R,I}$) tend to remain constant given the same chromatographic temperature program.

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Table 2a. Summary of Practical Quantitation Limits for Base/Neutral/Acid Semi-Volatile Organics[†]

COMPOUND	PQL _S (µg/kg)	PQL _W (µg/L)	IDL _S (µg/kg)	IDL _W (µg/L)	MDL _S (µg/kg)	MDL _W (µg/L)	PQL _S /IDL _S	PQL _W /IDL _W
Pyridine	330	10.0	18.6	0.559	24.9	0.8	17.9	17.9
N-Nitrosodimethylamine	330	10.0	12.7	0.380	32.4	0.6	26.3	26.3
2-Picoline	330	10.0	25.3	0.759	94.0	6.8	13.2	13.2
Methyl methanesulfonate	330	10.0	17.8	0.534	162.6	2.3	18.7	18.7
Ethyl methanesulfonate	330	10.0	9.0	0.271	150.1	3.8	36.8	36.8
Phenol **	330	10.0	14.6	0.439	278.0	4.0	22.8	22.8
Aniline	330	10.0	27.0	0.809	250.9	15.7	12.4	12.4
2-Chlorophenol **	330	10.0	14.8	0.443	261.4	3.6	22.6	22.6
Bis(2-chloroethyl)ether	330	10.0	7.9	0.238	247.3	4.4	42.0	42.0
1,3-Dichlorobenzene	330	10.0	15.9	0.476	226.3	5.1	21.0	21.0
1,4-Dichlorobenzene **	330	10.0	8.4	0.253	242.6	5.8	39.5	39.5
1,2-Dichlorobenzene	330	10.0	8.1	0.242	231.5	5.9	41.4	41.4
Bis(2-chloroisopropyl)ether	330	10.0	7.8	0.234	265.3	4.2	42.7	42.7
Benzyl Alcohol	330	10.0	10.9	0.328	307.0	4.5	30.5	30.5
Acetophenone	330	10.0	9.6	0.287	248.5	4.9	34.9	34.9
o-Cresol	330	10.0	8.3	0.249	257.4	3.3	40.1	40.1
p,m-Cresol	330	10.0	9.6	0.287	280.2	3.9	34.8	34.8
Hexachloroethane	330	10.0	13.0	0.390	222.5	4.3	25.7	25.7
N-Nitrosodi-n-propylamine*	330	10.0	11.2	0.336	305.9	5.5	29.8	29.8
Nitrobenzene	330	10.0	12.0	0.361	223.7	3.3	27.7	27.7
N-Nitrosopiperidine	330	10.0	15.7	0.471	243.3	4.0	21.2	21.2
Isophorone	330	10.0	10.1	0.304	238.6	4.0	32.9	32.9
2-Nitrophenol	330	10.0	59.8	1.793	208.3	4.0	5.6	5.6
2,4-Dimethylphenol	330	10.0	18.9	0.568	234.7	3.3	17.6	17.6
Bis(2-chloroethoxy)methane	330	10.0	13.2	0.397	232.1	4.3	25.2	25.2
2,4-Dichlorophenol	330	10.0	13.3	0.399	220.8	4.5	25.0	25.0
1,2,4-Trichlorobenzene **	330	10.0	16.5	0.494	209.0	4.1	20.2	20.2
Benzoic Acid	330	10.0	7.4	0.222	N/A	7.3	45.0	45.0
Naphthalene	330	10.0	12.7	0.380	222.2	4.9	26.3	26.3
4-Chloroaniline	330	10.0	118.1	3.542	307.7	9.2	2.8	2.8
2,6-Dichlorophenol	330	10.0	20.2	0.607	224.3	4.2	16.5	16.5
Hexachlorobutadiene	330	10.0	17.8	0.534	188.0	2.7	18.7	18.7
N-Nitroso-di-n-butylamine	330	10.0	17.8	0.535	256.1	4.6	18.7	18.7
4-Chloro-3-methylphenol **	330	10.0	12.6	0.377	264.8	4.2	26.5	26.5
2-Methylnaphthalene	330	10.0	14.4	0.433	223.4	4.5	23.1	23.1
1,2,4,5-Tetrachlorobenzene	330	10.0	22.2	0.667	197.6	3.5	15.0	15.0
Hexachlorocyclopentadiene	330	10.0	49.8	1.493	204.3	4.8	6.7	6.7
2,4,6-Trichlorophenol	330	10.0	16.1	0.483	212.0	3.2	20.7	20.7
2,4,5-Trichlorophenol	330	10.0	54.6	1.637	178.8	3.1	6.1	6.1
1-Chloronaphthalene	330	10.0	11.5	0.344	224.6	3.7	29.1	29.1
2-Chloronaphthalene	330	10.0	33.2	0.997	199.4	3.3	10.0	10.0
2-Nitroaniline	330	10.0	24.2	0.725	263.4	3.8	13.8	13.8
Acenaphthylene	330	10.0	40.4	1.212	247.1	3.4	8.3	8.3
Dimethyl Phthalate	330	10.0	10.2	0.305	322.0	3.8	32.8	32.8
2,6-Dinitrotoluene	330	10.0	24.4	0.732	315.2	3.9	13.7	13.7
3-Nitroaniline	330	10.0	27.8	0.833	368.1	5.1	12.0	12.0

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COMPOUND	PQL _S (µg/kg)	PQL _W (µg/L)	IDL _S (µg/kg)	IDL _W (µg/L)	MDL _S (µg/kg)	MDL _W (µg/L)	PQL _S /IDL _S	PQL _W /IDL _W
Acenaphthene **	330	10.0	17.0	0.509	398.5	3.1	19.6	19.6
2,4-Dinitrophenol	330	10.0	63.4	1.902	N/A	5.7	5.3	5.3
Dibenzofuran	330	10.0	17.4	0.522	385.9	3.5	19.1	19.1
4-Nitrophenol **	330	10.0	145.4	4.361	249.7	8.0	2.3	2.3
2,4-Dinitrotoluene **	330	10.0	20.9	0.628	276.9	3.5	15.9	15.9
1-Naphthylamine	330	10.0	54.0	1.619	460.8	24.9	6.2	6.2
2-Naphthylamine	330	10.0	130.3	3.908	442.8	30.8	2.6	2.6
2,3,4,6-Tetrachlorophenol	330	10.0	17.4	0.521	245.5	2.9	19.2	19.2
Fluorene	330	10.0	13.2	0.396	348.9	3.8	25.2	25.2
Diethyl phthalate	330	10.0	17.2	0.516	298.5	3.8	19.4	19.4
4-Chlorophenyl phenyl ether	330	10.0	12.5	0.376	365.0	4.2	26.6	26.6
4-Nitroaniline	330	10.0	210.8	6.323	340.7	5.7	1.6	1.6
4,6-Dinitro-2-methylphenol	330	10.0	20.6	0.619	142.9	3.5	16.2	16.2
N-Nitrosodiphenylamine	330	10.0	14.8	0.445	290.2	4.5	22.5	22.5
1,2-Diphenylhydrazine	330	10.0	10.9	0.326	333.3	4.3	30.7	30.7
Azobenzene	330	10.0	10.9	0.326	333.1	4.3	30.7	30.7
4-Bromophenyl phenyl ether	330	10.0	9.0	0.270	314.3	3.9	37.0	37.0
1,3,5-Trinitrobenzene	330	10.0	19.9	0.596	246.9	4.8	16.8	16.8
Phenacetin	330	10.0	17.2	0.517	185.5	4.2	19.3	19.3
Hexachlorobenzene	330	10.0	13.3	0.399	279.8	4.3	25.1	25.1
4-Aminobiphenyl	330	10.0	96.7	2.900	495.4	29.9	3.4	3.4
Pentachlorophenol **	330	10.0	15.8	0.474	176.0	2.9	21.1	21.1
Pronamide	330	10.0	14.0	0.419	273.4	5.1	23.9	23.9
Pentachloronitrobenzene	330	10.0	24.6	0.738	282.6	4.9	13.6	13.6
Phenanthrene	330	10.0	9.3	0.280	263.3	4.0	35.8	35.8
Anthracene	330	10.0	16.7	0.500	245.5	4.3	20.0	20.0
di-N-butyl phthalate	330	10.0	13.1	0.394	201.5	5.1	25.4	25.4
Fluoranthene	330	10.0	15.0	0.450	225.2	4.5	22.2	22.2
Benzidine	330	10.0	78.9	2.368	59.1	25.4	4.2	4.2
Pyrene **	330	10.0	7.3	0.219	260.1	5.0	45.7	45.7
p-Dimethylaminoazobenzene	330	10.0	14.0	0.421	229.7	4.3	23.8	23.8
Butyl benzyl phthalate	330	10.0	5.0	0.151	361.7	4.8	66.0	66.0
Benzo(a)anthracene	330	10.0	7.5	0.226	269.4	5.6	44.3	44.3
3,3'-Dichlorobenzidine	330	10.0	15.0	0.450	326.5	16.8	22.2	22.2
Chrysene	330	10.0	8.0	0.240	273.4	5.4	41.6	41.6
Bis(2-ethylhexyl)phthalate	330	10.0	12.8	0.384	481.3	5.5	26.0	26.0
Di-n-octyl phthalate	330	10.0	20.8	0.625	330.7	5.0	16.0	16.0
Benzo(b)fluoranthene	330	10.0	21.5	0.646	267.5	6.7	15.5	15.5
7,12-Dimethylbenz(a)anthracene	330	10.0	19.0	0.571	230.3	6.8	17.5	17.5
Benzo(k)fluoranthene	330	10.0	17.7	0.530	269.6	5.6	18.9	18.9
Benzo(a)pyrene	330	10.0	22.5	0.675	253.1	5.2	14.8	14.8
3-Methylcholanthrene	330	10.0	12.3	0.369	264.6	4.9	27.1	27.1
Dibenz(a,j)acridine	330	10.0	17.3	0.520	49.4	6.0	19.2	19.2
Indeno(1,2,3-cd)pyrene	330	10.0	15.5	0.465	262.2	6.0	21.5	21.5
Dibenzo(a,h)anthracene	330	10.0	19.1	0.574	254.9	6.5	17.4	17.4
Benzo(ghi)perylene	330	10.0	8.8	0.263	273.9	5.7	38.1	38.1

†: Data are from 08/08/2001 (IDL data) and 02/04/2002 (MDL data).

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Table 2b. Summary of Practical Quantitation Limits for Polynuclear Aromatic Semi-Volatile Organics[†]

COMPOUND	PQL _w (µg/L)	PQL _s (µg/kg)	IDL _w (µg/L)	IDL _s (µg/kg)	PQL _w /IDL _w	PQL _s /IDL _s
Naphthalene	5.0	330	0.957	31.9	5.2	10.4
2-Methylnaphthalene	5.0	330	0.478	15.9	10.5	20.9
Acenaphthylene	5.0	330	0.312	10.4	16.0	32.0
Acenaphthene	5.0	330	0.680	22.7	7.3	14.7
Fluorene	5.0	330	0.322	10.7	15.5	31.0
Phenanthrene	5.0	330	0.489	16.3	10.2	20.4
Anthracene	5.0	330	0.414	13.8	12.1	24.1
Fluoranthene	5.0	330	0.404	13.5	12.4	24.7
Pyrene	5.0	330	0.123	4.1	40.8	81.6
Benzo(a)anthracene	5.0	330	0.273	9.1	18.3	36.6
Chrysene	5.0	330	0.330	11.0	15.2	30.3
Benzo(b)fluoranthene	5.0	330	1.297	43.2	3.9	7.7
Benzo(k)fluoranthene	5.0	330	0.854	28.5	5.9	11.7
Benzo(a)pyrene	5.0	330	0.368	12.3	13.6	27.2
Indeno(1,2,3-cd)pyrene	5.0	330	0.300	10.0	16.7	33.4
Dibenzo(ah)anthracene	5.0	330	0.438	14.6	11.4	22.8
Benzo(ghi)perylene	5.0	330	0.624	20.8	8.0	16.0

[†]: Data are from 05/26/2001.

Table 2c. Practical Quantitation Limits for Diesel Range Organics[†]

COMPOUND	PQL _w (mg/L)	PQL _s (mg/kg)	IDL _w (mg/L)	IDL _s (mg/kg)	PQL _w /IDL _w	PQL _s /IDL _s
Diesel Range Organics	0.1	4	0.0078	0.26	15.5	12.9

[†]: Data are from 05/26/2001.

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Table 3. GC/MS Operating Conditions - Base/Neutral/Acid (BNA) and Polynuclear Aromatic (PNA) Semi-Volatile Organics Analysis[†]

Operating Parameter	BNA Analysis	PNA Analysis
Chromatographic Column	HP-5MS SV, <i>L</i> = 30 <i>m</i> , <i>ID</i> = 0.25 <i>mm</i>	HP-5MS SV, <i>L</i> = 30 <i>m</i> , <i>ID</i> = 0.25 <i>mm</i>
Carrier Gas	Helium (He) at 2 <i>ml/min</i>	Helium (He) at 2 <i>ml/min</i>
Temperature Program	<i>Variable-Instrument dependent</i>	<i>Variable-Instrument dependent</i>
Injector Temperature	250°C	250°C
Detector Temperature	280°C	280°C
Injection Volume	1-2 μ <i>l</i>	1 μ <i>l</i>
Mass Scanning Range	40 <i>m/z</i> - 450 <i>m/z</i>	35 <i>m/z</i> - 550 <i>m/z</i>
Mass Scanning Rate	1.8 <i>Hz</i>	1.4 <i>Hz</i>

[†]: Note that DROs may be analyzed by either of the two sets of operating conditions.

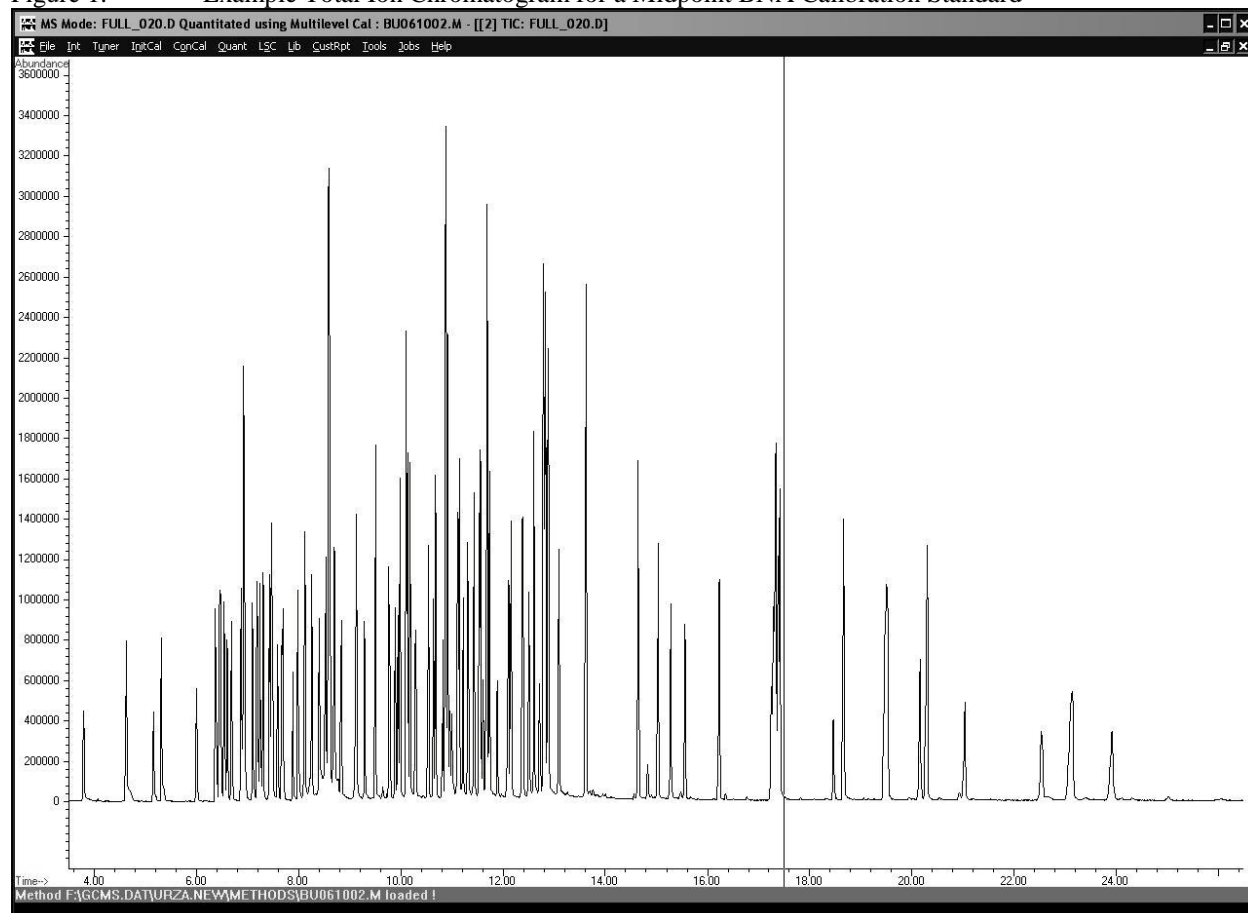
Table 4. DFTPP Tune Evaluation Criteria

Target <i>m/z</i>	Relative <i>m/z</i>	LCL (%)	UCL (%)
51	198	30.0	80.0
68	69	0.0	2.0
69	198	0.0	NA
70	69	0.0	2.0
127	198	25.0	75.0
197	198	0.0	1.0
198	198	100.0	100.0
199	198	5.0	9.0
275	198	10.0	30.0
365	198	1.0	NA
441	443	0.0	100.0
442	198	40.0	110.0
443	442	15.0	24.0

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Revision: 10
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Figure 1. Example Total Ion Chromatogram for a Midpoint BNA Calibration Standard[†]

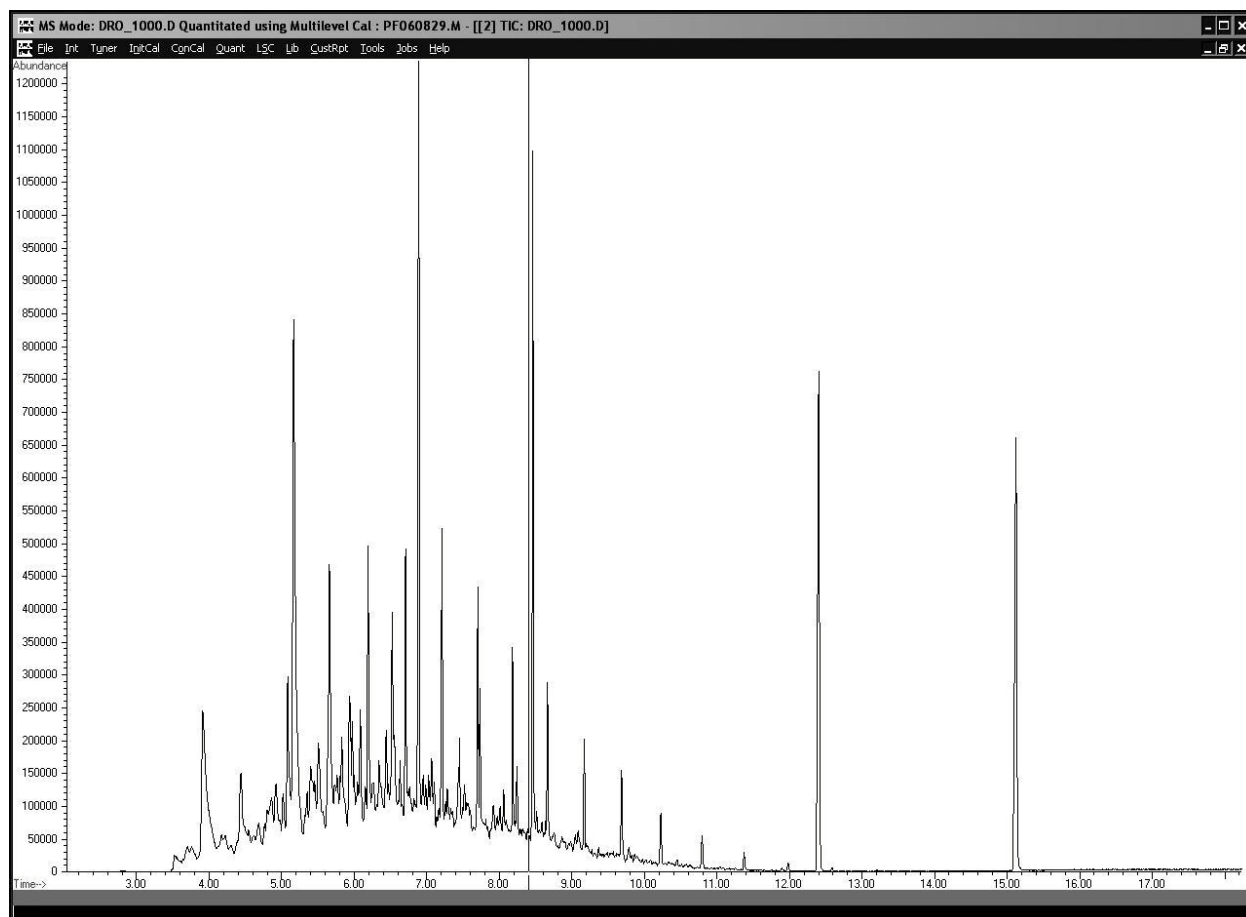


[†]: Data file FULL_020.D from calibration BU061002.M (20 ng/μL). GC/MS acquisition parameters are given by Table 4 for BNA Analysis.

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Figure 2. Example Total Ion Chromatogram for a Diesel Range Organics Calibration Standard[†]



[†]: Data file DRO_1000.D from calibration PD061007.M (1.0 g/L). GC/MS acquisition parameters are given by Table 4.

Location: PCB Laboratory (Sample analysis)
Extraction Laboratory (sample extraction and clean-up procedures)

This method is restricted to use by, or under the supervision of trained analysts experienced in the use of gas chromatographs (GC) and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method as well as a working knowledge of Chrom Perfect and the PCB calculator software.

1.0 SCOPE AND APPLICATION

- 1.1 This method is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in extracts from solid and aqueous matrices. Open-tubular, capillary columns are employed with electron capture detectors (ECD). The target compounds listed below may be determined by a dual-column analysis system.

Parameter	CAS #:
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

1.2 Aroclors are multi-component mixtures. When samples contain more than one Aroclor, a higher level of analyst expertise is required to attain acceptable levels of qualitative and quantitative analysis. The same is true of Aroclors that have been subjected to environmental degradation ("weathering") or degradation by treatment technologies. Such weathered multi-component mixtures may have significant differences in peak patterns than those of Aroclor standards. Quantitation of PCBs as Aroclors is appropriate for many regulatory compliance determinations, but is particularly difficult when the Aroclors have been weathered by long exposure in the environment.

- 1.3 This method also includes different clean-up procedures used to assist in removing some of the more common found interferences.
- 1.4 This method describes a dual-column GC set up for the determination of total PCB Aroclor concentrations. A hardware configuration of two analytical columns joined to a single injection port is utilized.
- 1.5 The MDLs for Aroclors are determined annually on all instruments analyzing PCBs. Estimated quantitation limits are determined using the referenced SW 846 Method 8082, Table 1, specifically Table 4 for the data generated by this laboratory.

2.0 SUMMARY OF METHOD

- 2.1 A measured volume or weight of sample (approximately 1 L for liquids, 20 g for soil, and 0.3 g for oil samples) is extracted using the appropriate matrix-specific sample extraction technique^[1].

Note: Unusually contaminated samples may be extracted with lower sample amounts. The reporting limits are corrected accordingly. Sample specific notes are added and samples flagged.

- 2.2 Aqueous samples are extracted at neutral pH with methylene chloride using 3510pcb SOP (separatory funnel)
- 2.3 Solid samples are extracted with hexane using Method 3550pcb SOP (ultrasonic)
- 2.4 Extracts for PCB analysis are subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665) designed specifically for PCBs. This cleanup technique will remove (destroy) many single component

^[1] Reference for this procedure is SW-846, Revision 3, December 1996 Method 3510C, Liquid Liquid Separatory Funnel Extraction, and, Method 3550C, Ultrasonic Extraction.

organochlorine or organophosphorus pesticides. Therefore, the analysis of pesticides is not converted by this SOP.

- 2.5 After the acid clean-up, a sulfur clean-up (§ 7.2) is performed. The activated copper reacts with the sulfur interference to form a precipitate (ex. $2\text{RSH} + \text{Cu}^{++} \rightarrow \text{Cu}(\text{SR})_2 + 2\text{H}^+$, where R is the organic radical and SH is the mercaptan radical).
- 2.6 After the clean-up procedures, the extract is analyzed by injecting a 1-2 uL aliquot into a gas chromatograph with narrow-bore fused silica capillary column and electron capture detector (GC/ECD).
- 2.7 The chromatographic data may be used to determine the seven Aroclors in § 1.1

3.0 INTERFERENCES

- 3.1 Interferences co-extracted from the samples will vary considerably from matrix to matrix. While general cleanup techniques are provided, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation. Sources of interference in this method can be grouped into three broad categories.
 - 3.1.1 Contaminated solvents, reagents, or sample processing hardware.
 - 3.1.2 Contaminated GC carrier gas, parts, column surfaces, or detector surfaces.
 - 3.1.3 Compounds extracted from the sample matrix to which the detector will respond.
- 3.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in PCB determinations.
 - 3.2.1 Common flexible plastics contain varying amounts of phthalate esters that are easily extracted or leached from such materials during laboratory operations. Interferences from phthalate esters are minimized by avoiding contact with any plastic materials and checking all solvents and reagents for interferences.
 - 3.2.2 Exhaustive cleanup of solvents, reagents, and glassware may be required to eliminate background phthalate ester contamination. These materials can be removed through the use of procedure described in §7.2 (sulfuric acid/permanaganate cleanup), which is required for all PCB analysis.
 - 3.2.3 Cross-contamination of clean glassware is avoided by scrupulously cleaning and then baking glassware in a 550°C oven for 4 – 12 hours.
 - 3.2.3.1 Clean all glassware as soon as possible after use by rinsing with the last solvent used. This is followed by detergent washing with hot water, and rinses with tap water and DI water. Drain the glassware, and let dry for several hours, or rinse with methanol and drain. Store dry glassware in a clean environment.
 - 3.2.3.2 Elemental sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur is removed using procedure described in § 7.2).

4.0 APPARATUS AND MATERIALS

- 4.1 Gas chromatograph - An analytical system complete with a gas chromatograph suitable for on-column and split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and a data system.
- 4.2 GC columns - The dual-column arrangement used by this method involves a single injection that is split between two columns mounted in a single gas chromatograph. Each column is connected to a separate ECD detector.
 - 4.2.1 Narrow-bore columns are installed in split/splitless (Grob-type) injectors.
 - 4.2.2 30m x 0.25mm ID fused silica capillary column chemically bonded with SE-54 (DB-5, 0.25um film thickness).

- 4.2.3 30m x 0.25mm ID fused silica capillary column chemically bonded with 35 percent phenyl methylpolysiloxane (DB-608, 0.25um film thickness)
- 4.2.4 Column pair is mounted in a press-fit Y-shaped glass 3-way fused-silica connector (Supelco)
- 4.2.5 Column rinsing kit - Bonded-phase column rinse kit
- 4.2.6 Glass vials for both sample storage, cleaning, and standard preparation.
- 4.2.7 Hamilton Syringes (1ul to 1000 ul)
- 4.2.8 Sample Vials: 1.8 ml screw cap with PTFE liner and 4.0 ml calibrated screw cap

5.0 REAGENTS

- 5.1 Reagent grade or pesticide grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

Note: Store the standard solutions (stock, composite, calibration, internal, and surrogate standards) at 4°C in polytetrafluoroethylene (PTFE)-sealed amber containers, or in a dark area. When a lot of standards is prepared, the aliquots of that lot are stored in individual small vials. All stock standard solutions are replaced every 12 months or sooner depending if the QC indicates a problem. All working standard solutions are replaced after six months or sooner if routine QC indicates a problem.

- 5.2 Sample extracts are prepared by liquid - liquid extraction (3510pcb SOP) for waster samples or ultrasonic extraction (3550pcb SOP) for solid and oil samples. Both procedures undergo a solvent exchange step prior to analysis. The following solvents are necessary for dilution of sample extracts. All solvent lots should be pesticide quality or equivalent.

- 5.2.1 n-Hexane, C₆H₁₄
- 5.2.2 Methanol, CH₃OH
- 5.2.3 Acetone, CH₃COCH₃

5.3 DI Water

- 5.4 Stock standard solutions (1000 mg/L) Commercially prepared stock standard solutions are used. All standards that are purchased must be certified by the manufacturer or by an independent source.

5.5 Calibration standards for Aroclors

- 5.5.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 includes many of the peaks represented in the other five Aroclor mixtures. A multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations demonstrates the linearity of the detector response without the necessity of performing initial calibrations for each of the seven Aroclors.
- 5.5.2 The 1016/1260 mixture is used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Prepare a minimum of five calibration standards containing equal concentrations of both Aroclor 1016 and Aroclor 1260 by dilution of the stock standard with hexane. The curve concentrations bracket the linear range of the detector. (0.1 to 1.0 ppm, see Table 7; Also see Table 8 for standard preparation).
- 5.5.3 Method 8082 states that: *“Single standards of each of the other five Aroclors are required to aid the analyst in pattern recognition. Assuming that the Aroclor 1016/1260 standards have been used to demonstrate the linearity of the detector, these single standards of the remaining five Aroclors are also used to determine the calibration factor for each Aroclor...The concentrations should correspond to the mid-point of the linear range of the*

detector.” At this time, a 5-point calibration curve for each Aroclor is employed. During a sample batch, if an Aroclor is identified in a sample, a standard of that Aroclor is analyzed. If the standard concentration falls within the control limits for that Aroclor, the sample is quantitated using the 5-point curve for that Aroclor.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 6.1 All samples are sampled using 1L Amber glass jars or 4 –8 oz. glass jars for solids. Oil and wipe samples must only be collected in glass jars. (No plastic containers should be used, see §3.2)
- 6.2 Extracts are stored under refrigeration at 4°C and are analyzed within 40 days of extraction.

7.0 PROCEDURE

- 7.1 Samples are extracted using the 3510PCB SOP and 3550PCB SOP.

- 7.1.1 Water samples are extracted at a neutral pH with methylene chloride using a separatory funnel
- 7.1.2 Solid samples are extracted with ultrasonic extraction.
- 7.1.3 Spiked samples are used to verify the applicability of the selected extraction technique for each new sample type (*i.e.* water, soil, oil, *etc.*). These samples are spiked with Aroclor 1016/1260 mixture at 0.500 mg/l concentration.

- 7.2 Extract clean-ups (MANDATORY FOR ANALYSIS AND QC SAMPLES)

- 7.2.1 **Sulfuric Acid Clean-up**^[2]: This method is suitable for the rigorous cleanup of sample extracts prior to analysis for polychlorinated biphenyls. This method is used to reduce elevated baselines in overly complex chromatograms that prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.
 - 7.2.1.1 Place up to 3 ml of concentrated sulfuric acid into the final hexane extract 4 ml vial. Make sure this is done only in the hood area. Safety glasses should be worn at all times.
 - 7.2.1.2 Place the cap on the vial and shake the extract with the acid. The acid will dissolve and carbonize the interferences commonly found in PCB samples.
 - 7.2.1.3 Blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them.
 - 7.2.1.4 If the acid is “carbonized” or turns a dark brown color, new fresh acid can be added. Potassium Permanganate (KMnO₄) can be used when the sulfuric acid capacity is exceeded as an oxidizing reagent
- 7.2.2 **Sulfur Clean-up**^[3]: This clean-up is performed at the GC laboratory station. Elemental sulfur is encountered in many liquid and sediment samples (commonly found in industrial wastes). The solubility of sulfur in various solvents is very similar to the organochlorine compounds of interest. Therefore, the sulfur interference follows along with the target compounds through the normal extraction and Florisil cleanup techniques. Sulfur will be quite evident in gas chromatograms obtained from electron capture detectors.

^[2] Reference for Sulfuric Acid clean-up is SW-846, Revision 3, December 1996 Method 3665A: Sulfuric Acid

^[3] Reference for Sulfur clean-up is SW-846, Revision 3, December 1996 Method 3660B: Sulfur Clean-up using copper.

- 7.2.2.1 Add approximately 1g of high grade, activated copper shots or copper powder to the final hexane sample extract. The activated copper is prepared by rinsing the copper with diluted nitric acid, rinsed with acetone and dried before use.
- 7.2.2.2 Vortex for 1 minute. Allow the copper to settle to the bottom. If a high precipitate occurs, the sample can be centrifuged. If the copper seems to be saturated, more can be added.
- 7.2.2.3 If copper powder is used, follow steps 7.2.2.1 – 7.2.2.2 and then carefully transfer the “cleaned” extract into another vial to prevent the “powder” from plugging up the auto syringe.

7.3 **Alumina Clean-up** is an adsorption technique used when the chromatogram base line is still elevated after the two clean-up procedures listed above were performed. Alumina clean-up^[4] is used to separate the high molecular weight petroleum wastes from PCBs using liquid chromatography.

- 7.3.1 Alumina Column Clean-up: the column is packed with the required amount of adsorbent, topped with a water adsorbent (Na_2SO_4), and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s), leaving the interfering compounds on the column. The elute is then concentrated (if necessary).
- 7.3.2 Place a clean glass wool plug in the bottom of a 50 ml disposable chromatographic column.
 - 7.3.2.1 On top of this plug, add 2 cm of anhydrous Na_2SO_4 and tap it down.
- 7.3.3 Pour about 10 g of activated (130°C for 12 hours) Alumina (150 mesh) into the column.
- 7.3.4 Tap it down and place 2 cm of anhydrous (130°C for 12 hours) Na_2SO_4 on top of the Alumina.
- 7.3.5 Rinse the column with 40 ml hexane and place the eluted hexane in a bottle labeled “Clean Used Hexane”.
- Note The column should not be allowed to become dry throughout the rest of the analysis. The disposable column will stop flowing naturally when the solvent level is at the top of the Na_2SO_4 .*
- 7.3.6 Weigh 0.3 g of oil (3%-5% of Alumina weight) and dissolve it in 2 ml hexane. *Note: This oil solution can be treated with concentrated H_2SO_4 before advancing to the next step.*
- 7.3.7 Using a long pasture pipette, place it on the column followed by rinse of the sample vial and the column with 2 ml hexane.
- 7.3.8 Place Azulene (400 mg/L in hexane) on the column. Azulene is a blue color indicator to help visually to follow the sample through the column. To make the Azulene solution, weigh 50 mg of high purity Azulene powder to 125 ml hexane.
- 7.3.9 Wash the column with 10 ml hexane and place the eluted hexane in a bottle labeled “Dirty Used Hexane”. This washes the aliphatic interferences out of the sample.
- 7.3.10 Place surrogate standard mixture (in hexane – not methanol) on the column and rinse with 1 ml hexane.
- 7.3.11 Elute 80 ml 6% ethyl ether in hexane through the column and collect it for the analysis of PCBs and/or Pesticides.
- 7.3.12 Concentrate the eluted hexane from step 7.3.11 to 0.5 ml inside the Zymark Evaporation Station.

^[4] Reference for Alumina clean-up is SW-846, Revision 3, December 1996 Method 3611B: Alumina Column Clean-up & Separation of Petroleum Products.

- 7.3.13 Transfer it quantitatively to a graduated 4 ml vial rinsing the evaporating tube with 0.5 ml hexane, bringing the volume of cleaned sample in the vial to 1 ml.
- 7.3.14 Add 3 – 4 ml H₂SO₄ (concentrated) to the vial cap and shake. *Note: this carbonizes and dissolves much of the remaining interfering compounds.*

7.4 GC conditions

- 7.4.1 **Dual-column analysis:** The dual-column/dual-detector has two 30m x 0.25mm ID fused-silica open-tubular columns of different polarities, and thus has different selectivities towards the target compounds. The columns are connected to an injection tee and ECD detectors. For types of columns see Table 1.
- 7.4.2 GC temperature programs and flow rates are listed in Table 1.

7.5 Calibration

- 7.5.1 Prepare calibration standards as described in the standard preparation logbook for PCBs/Pesticides (See Table 7). Both initial calibration and calibration verification standards are prepared using two different vendors to insure the quality and correctness of the standards.

Note: Prior to calibration, GC operating conditions should be established which optimize both peak resolution and sensitivity. The total run time should be long enough permit the elution of the second surrogate standard (DCBP). Once established, the same operating conditions must be used for both calibrations and sample analyses.

Note: Because of the sensitivity of the electron capture detector, the injection port and column should always be cleaned prior to performing the initial calibration.

- 7.5.2 PCBs are quantitatively determined as Aroclors. The initial calibration consists of the following protocols:

- 7.5.2.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Therefore, this mixture of 1016/1260 is used to demonstrate the linearity of the detector (RPD value of the curve) and that a sample does *not* contain peaks that represent any one of the Aroclors. This standard is also used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, if they are present in a sample. Therefore, an initial five-point calibration is performed using the mixture of Aroclors 1016 and 1260.

- 7.5.2.2 Standards of the other five Aroclors are necessary for pattern recognition. SW 846 states: “*These standards are also used to determine a single-point calibration factor for each Aroclor... The Aroclor 1016/1260 mixture is used to determine correct detector response. The standards for the remaining five Aroclors are analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five 1016/1260*”.

- 7.5.2.3 A 5-point initial calibration for each of the 5 Aroclors is established. As long as a calibration verification standard at a midpoint concentration passes within the required control limits, samples are analyzed after the standard and computed based upon a 5-point calibration. In situations where only a few Aroclors are of interest for a specific project, the analyst can use a five-point initial calibration of each of the Aroclors of interest (*e.g.*, five standards of Aroclor 1254 if this Aroclor is of concern) and not use the 1016/1260 mixture.

- 7.5.3 An auto sampler is used to inject 1-2uL volumes of each calibration standard. Depending on the volume of sample injected (*i.e.* 1 or 2 uL), the initial calibration, the QC samples, and samples must be analyzed with the same injection volume.

- 7.5.4 Record the peak area for each characteristic Aroclor peak to be used for quantitation using the Chrom Perfect Software.
- 7.5.5 A minimum of 3 peaks is chosen for each Aroclor, and preferably 5 peaks (See Table 2 for Quantification Peaks). The peaks are characteristic of the Aroclor in question. If possible, choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the Aroclor 1016/1260 mixture, none of which should be found in both of these Aroclors.
- 7.5.6 Tables 2a and 2b list recommended diagnostic peaks in each Aroclor, along with their retention times on two GC columns suitable for dual-column analysis.
- 7.5.7 Calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the equation below.

$$CF = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in nanograms)}}$$

- 7.5.8 Calibration factors from the initial calibration are used to evaluate the linearity of the initial calibration. The PCB calculator initial calibration report is generated which involves the calculation of the mean calibration factor, the standard deviation, and the relative standard deviation (RSD) for each Aroclor. The RSD for a given calibration range must be $\leq 20\%$ in order to employ the calibration method described in § 7.5.7 ^[5]
- 7.5.9 A better representation of the calibration data may be obtained by narrowing the calibration range (by lowering the upper level standard) or by using a least-squares regression in accordance with SW-846, Method 8000. A linear regression may be used with a 5-point calibration curve, and the C.O.D. must be > 0.99 . Additional standards must be analyzed in order to utilize a non-linear calibration (*see* Method 8000). All least-squares regressions used for OHIO VAP analysis will use a calculated intercept and quadratic fits will only be used for compounds exhibiting nonlinear behavior.

7.6 Retention Time Windows

~~7.6.1~~ 7.6.1.1 Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for the identification of PCBs as Aroclors. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loading and normal chromatographic variability. The width of the retention time window is established by analyzing successive calibration standards of the same Aroclor mixture. The standard deviation (σ) of these repeated measurements is used to determine this window. The window is defined as the mean retention time $\pm 3\sigma$. The results of this analysis are contained in Table 3. Given that the maximum window for an individual PCB is approximately 0.08 min., a nominal identification window of 0.1 minutes is utilized for all PCBs.

~~7.7.1~~ 7.7.1.7 Gas chromatographic analysis of sample extracts

~~7.7.1.1~~ 7.7.1.7.1 The same GC operating conditions used for the initial calibration are used for sample analyses and calibration verification.

^[5] Reference for RSD values is SW-846, Revision 3, December 1996 Method 8000B Determinative Chromatographic Separations

~~7.7.2~~7.7.1.7.2 An analytical sequence of laboratory samples and QC samples should be templated after the following:

- Calibration verification mixture (1016/1260)
- Laboratory control sample
- Blank
- Reagent Blank
- Up to 20 samples
- Duplicate sample
- Matrix spike and/or matrix spike duplicate sample
- Batch-terminating standard

~~7.7.3~~7.7.1.7.3 Verify the calibration each 12-hour shift by injecting a calibration verification standard prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than once every twenty samples. The calibration verification standard is a mixture of Aroclor 1016 and Aroclor 1260 from a different source than the initial calibration standards.

~~7.7.4~~7.7.1.7.4 The calibration factor for each analyte calculated from the calibration verification standard (CF_v) must not exceed a difference of more than $\pm 15\%$ when compared to the mean calibration factor from the initial calibration curve:

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

~~7.7.5~~7.7.1.7.5 Corrective action: if this criterion is exceeded for any calibration factor, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis. If routine maintenance does not return the instrument performance to meet the QC requirements based on the last initial calibration, then a new initial calibration must be performed. Please refer to Table 9 Quality Control Items, Frequency and Corrective Action

~~7.7.6~~7.7.1.7.6 Inject a 1-2 uL (See §7.5.3) aliquot of the concentrated sample extract.

~~7.7.7~~7.7.1.7.7 Qualitative identifications of target analytes are made by examination of the sample chromatograms, as described in §7.8.

~~7.7.8~~7.7.1.7.8 Quantitative results are determined for each identified Aroclor, using the procedures described in §7.9. If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze.

~~7.7.9~~7.7.1.7.9 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour shift), or calibration standards interspersed within the samples. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be re-injected.

~~7.7.10~~7.7.1.7.10 A batch of 20 sample injections (including QC samples, see above) may continue as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. A smaller batch than 20 samples can be analyzed in order to minimize the number of samples that must be re-injected if the standards fail the QC limits. The sequence ends when the set of samples has been injected or when quantitative QC criteria are exceeded.

~~7.7.11~~7.7.1.7.11 If the peak response is less than 2.5 times the baseline noise level, the validity of the quantitative result may be questionable. The analyst should consult with the source of the sample to determine whether further concentration of the sample or additional clean-ups are warranted.

~~7.7.12~~7.7.12 Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.

~~7.8.1~~7.8.1 Qualitative Identification (The equations governing the quantification, recovery and precision are referenced in the glossary section of the QA/QC manual)

~~7.8.1.8.1~~7.8.1.8.1 The identification of PCBs as Aroclors using this method with an electron capture detector is based on agreement between the retention times of peaks in the sample chromatogram with the retention times and windows established through the analysis of standards of the target analytes (*see* Tables 2a, 2b, and 3).

~~7.8.2~~7.8.21.8.2 Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Each tentative identification is confirmed using a second GC column of dissimilar stationary phase (as in the dual-column analysis), based on a clearly identifiable Aroclor pattern. The second column is calibrated and utilized for purposes of qualitative identification only.

~~7.8.3~~7.8.31.8.3 Tentative identification of an Aroclor pattern is based upon an approximate match of the relative characteristic peak heights between the sample and reference standard. Use the individual Aroclor standards (not the 1016/1260 mix) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, and 1254. The patterns for Aroclors 1016 and 1260 are evident in the mixed calibration standards (See Figure 1).

~~7.8.4~~7.8.41.8.4 Positive identifications require a second column confirmation. Both QC samples and calibrations are verified with the second (confirmation) column.

~~7.9.1~~7.9.1 Quantitation of PCBs

~~7.9.1.9.1~~7.9.1.9.1 The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

~~7.9.2~~7.9.21.9.2 The characteristic quantitative peaks for each Aroclor are listed in Tables 2a and 2b and illustrated in Figure 1. The amount of Aroclor is calculated using the 5-point calibration curve for each of the 3 to 5 characteristic peaks chosen. The concentration is determined using the average concentration for each of the characteristic peaks.

~~7.9.3~~7.9.31.9.3 In the event that the data system is unable to properly integrate the peaks of interest (typically due to peak co-elution or matrix interference), a manual integration procedure is performed. The applicability, procedure, and documentation of the manual integration are addressed in the SOP *Manual Integration of Chromatographic Data*.

~~7.9.4~~7.9.41.9.4 Compound identifications are supported by at least one additional qualitative technique (i.e., second column confirmation).

~~7.9.4.1~~7.9.4.11.9.4.1 For Ohio VAP samples, both columns must meet the calibration and QC criteria.

~~7.9.5~~7.9.51.9.5 The second column quantitation can be applied upon request to any project. In this case, all QC requirements listed above are applied to each set of chromatographic data. PCB concentrations from each column are reported.

Note: Weathering of PCBs in the environment and changes resulting from waste treatment processes may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems.

~~7.10~~7.101.10 Chromatographic System Maintenance as Corrective Action

~~7.10.1~~1.10.1 When system performance does not meet the established QC requirements, corrective action is required, and may include one or more of the following.

~~7.10.1.1~~1.10.1.1 Splitter connections for dual columns which are connected using a press-fit a Y-shaped fused-silica connector, clean and deactivate the splitter port insert or replace with a cleaned and deactivated splitter. Break off the first few inches (up to one foot) of the injection port side of the column. Remove the columns and solvent back-flush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the columns.

~~7.10.2~~1.10.2 Metal injector body

~~7.10.2.1~~1.10.2.1 Turn off the oven and remove the analytical columns when the oven has cooled. Remove the glass injection port insert (instruments with on-column injection). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

~~7.10.2.2~~1.10.2.2 Place a beaker beneath the injector port inside the oven. Using a wash bottle, rinse the entire inside of the injector port with acetone and then rinse it with toluene, catching the rinsate in the beaker.

~~7.10.2.3~~1.10.2.3 Consult the manufacturer's instructions regarding deactivating the injector port body. Glass injection port liners may require deactivation with a silanizing solution containing dimethyldichlorosilane.

~~7.10.3~~1.10.3 Column rinsing

~~7.10.3.1~~1.10.3.1 The column should be rinsed with several column volumes of an appropriate solvent. Both polar and non polar solvents are recommended. Depending on the nature of the sample residues expected, the first rinse might be water, followed by methanol and acetone. Methylene chloride is a good final rinse and in some cases may be the only solvent required. The column should then be filled with methylene chloride and allowed to stand flooded overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultra-pure nitrogen.

8.0 QUALITY CONTROL AND METHOD PERFORMANCE

8.1 Quality control procedures necessary to evaluate the GC system operation include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.2 The QC Reference Sample is a sample that is analyzed prior to any analysis to demonstrate the initial proficiency of the analyst or the instrument. In cases when a new instrument is introduced or a new analyst, this sample when analyzed within the control limits of $\pm 20\%$ demonstrates the initial proficiency of the method. The QC reference sample should be spiked with in the linear calibration range. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260.

8.3 Method Detection Limit (MDL). The MDL is determined for each of the PCB Aroclors as specified in the QA/QC manual. The results of this study for the past three years are given in Table 4. A new MDL study is performed annually for each Aroclor.

~~8.4~~1.4 Accuracy & Precision - Accuracy & Precision are determined for sample matrices of interest by computing the mean recovery and relative standard deviation of the LCS analysis. The upper and lower control limits for matrix spike recovery are determined as the mean $\pm 3\sigma$. The results for the water and solid matrices are given in Table 5.

~~8.5.1.5~~ The Continuing Calibration Verification (CCV) concentrate should contain PCBs as Aroclors at mid point of the curve. If Aroclors are not expected in samples from a particular source, then prepare the QC reference samples with a mixture of Aroclors 1016 and 1260. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for the CCV.

~~8.5.1.1.1~~ The frequency of analysis of the CCV analysis is equivalent to a minimum of 1 per 12 hours not to exceed 20 samples between CCVs. A closing calibration verification is required at the end of the run.

~~8.5.2.1.2~~ If the averaged recovery of compounds found in the CCV is less than 85% or greater than 115% of the true value, the laboratory performance is judged to be out of control, and the problem must be corrected. Please refer to Table 9 Quality Control Items, Frequency and Corrective Action

~~8.5.3.1.3~~ [A new set of calibration standards should be prepared and analyzed.

~~8.5.4.1.4~~ Include a calibration standard after each group of 20 samples. The response factors for the calibration should be within 15 percent of the initial calibration. When this continuing calibration is out of this acceptance window, the laboratory should halt the analysis and take corrective action. Please refer to Table 9 Quality Control Items, Frequency and Corrective Action

~~8.6.1.6~~ Sample Quality Control for Preparation and Analysis – A batch includes the analysis of QC samples including a method blank, a matrix spike, matrix spike duplicate and/or a duplicate (per client request), and a laboratory control sample (LCS). Surrogates are added to each field and QC sample.

~~8.6.1.6.1~~ Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair, spiked with the Aroclor 1016/1260 mixture. However, when specific Aroclors are known to be present or expected in samples, the specific Aroclors should be used for spiking. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample.

~~8.6.2.1.6.2~~ If a sample is qualitatively identified as having an Aroclor which was *not* analyzed as part of the QC samples, the sample is subsequently re-analyzed along with a calibration check standard of the appropriate type.

~~8.6.3.1.6.3~~ A Laboratory Control Sample (LCS) is included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

~~8.7.1.7~~ Surrogate recoveries - Surrogate recovery data is analyzed from individual samples in order to determine matrix-specific control limits. The surrogate standard must contain the following compounds TCX (tetrachloro-m-xylene) and DCBP (decachlorobiphenyl). The surrogate standard is prepared by the GC analyst at a concentration of 0.03mg/l. and utilized by the extraction analyst. Table 6 contains surrogate recovery data and laboratory-established control limits, and is inclusive of the effect of copper and sulfuric acid clean-up procedures. The surrogate standards are calibrated using a 5-point curve.

~~8.8.1.8~~ The MS/MSD and LCS spikes contain a mixture of Aroclor 1016/1260. This spike should be prepared at a concentration at or below the medium level of the PCB curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.5mg/l.

9.0 APPENDICES

Table 1. GC Operating Conditions For PCBs As Aroclors (Dual Column)

<i>Property</i>	<i>Setting</i>
Column #1	DB-5, 30m x 0.25mm ID, 0.25µm film thickness
Column #2	DB-608, 20 m x 0.25 mm ID, 0.25 µm film thickness
Carrier gas flow (He)	6ml/min
Makeup gas flow (N ₂)	20ml/min
Temperature program	T _o = 180°C, hold 1.0min 180°C to 250°C, ramp at 6.0°C/min T _f = 250°C, hold 2.34min
Injector temperature	250°C
Detector temperature	320°C
Injection volume	1-2 µl, no air plug
Solvent	Hexane
Injector	On-column
Detector	Dual ECD
Range attenuation	10/8
Splitter	Supelco press-fit Y-shaped inlet splitter

Table 2a. Summary of Characteristic PCB Peak Retention Times (DB-5 Column)[†]

<i>Peak</i>	<i>1016</i>	<i>1221</i>	<i>1232</i>	<i>1242</i>	<i>1248</i>	<i>1254</i>	<i>1260</i>
1	1.85	[‡] 1.73	1.71	1.84	2.30	3.45	5.08
2	[‡] 2.30	[‡] 1.82	[‡] 1.86	[‡] 2.30	[‡] 2.90	4.63	6.46
3	[‡] 2.53	[‡] 1.88	2.32	[‡] 2.53	3.06	[‡] 5.11	[‡] 7.07
4	[‡] 2.89	2.93	2.55	[‡] 2.89	3.44	5.69	7.37
5	[‡] 3.05		[‡] 2.91	[‡] 3.04	[‡] 3.80	[‡] 5.92	[‡] 7.75
6	3.16		[‡] 3.06	3.16	[‡] 4.02	[‡] 6.53	8.18
7	[‡] 4.01		[‡] 3.18	[‡] 4.00	[‡] 4.61	7.14	8.77
8			4.02	4.94	[‡] 4.96	[‡] 7.78	[‡] 9.54
9			4.96		5.91	8.47	[‡] 10.30
10							12.07

Table 2b. Summary of Characteristic PCB Peak Retention Times (DB-608 Column)[†]

<i>Peak</i>	<i>1016</i>	<i>1221</i>	<i>1232</i>	<i>1242</i>	<i>1248</i>	<i>1254</i>	<i>1260</i>
1	2.58	2.32	2.30	2.58	4.00	6.64	7.93
2	3.26	2.52	2.60	3.25	4.69	7.61	8.37
3	4.29	2.61	3.27	3.99	5.35	7.90	8.76
4	4.55		4.02	4.28	6.08	8.36	9.26
5	5.34		4.31	4.53	6.20	8.79	9.86
6			4.56	6.06	6.84	9.44	10.05
7			6.08	6.82	7.89	9.90	10.98
8			6.84		8.34		11.53
9							12.75
10							

[†]: Based upon data from 09/99 to 10/99 (see \PCB*.CAL); retention times given in minutes.[‡]: Quantitation peak.

Table 3. Retention Time Extraction Windows[†]

<i>Aroclor</i>	<i>n</i>	<i>σ (min)</i>	<i>Window (min)</i>
PCB-1016	204	0.0196	±0.0558
PCB-1221	n/a		
PCB-1232	n/a		
PCB-1242	238	0.0275	±0.0825
PCB-1248	48	0.0244	±0.0732
PCB-1254	120	0.0220	±0.0660
PCB-1260	120	0.0140	±0.0420
Cumulative Window – All PCBs	730	0.0219	±0.0657

[†]: Based upon data from 06/99 to 09/99 (see PCB_STD.XLS).Table 4. PCB Method Detection Limit Studies (all units in ppb)[†]

<i>Aroclor</i>	<i>Year</i>	<i>IDL</i>	<i>MDL – water</i>	<i>MDL – soil</i>	<i>PQL – water</i>	<i>PQL – soil</i>
PCB-1016	1998	0.02			0.1	330
	1999	0.05			0.1	330
	2000	0.008			0.1	330
	2001	0.02			0.1	330
	2003	0.008			0.1	330
	2004		0.1	3	0.1	330
PCB-1221	1998	0.04			0.1	330
	1999	0.03			0.1	330
	2000				0.1	330
	2001	0.008			0.1	330
	2003	0.01			0.1	330
	2004		0.05	2	0.1	330
PCB-1232	1998	0.02			0.1	330
	1999	0.06			0.1	330
	2000				0.1	330
	2001	0.02			0.1	330
	2003	0.007			0.1	330
	2004		0.06	4	0.1	330
PCB-1242	1998	0.04			0.1	330
	1999	0.09			0.1	330
	2000	0.03			0.1	330
	2001	0.009			0.1	330
	2003	0.006			0.1	330
	2004		0.1	3	0.1	330
PCB-1248	1998	0.06			0.1	330
	1999	0.04			0.1	330
	2000	0.02			0.1	330
	2001	0.02			0.1	330
	2003	0.006			0.1	330
	2004		0.1	4	0.1	330
PCB-1254	1998	0.03			0.1	330
	1999	0.06			0.1	330
	2000	0.01			0.1	330
	2001	0.02			0.1	330
	2003	0.01			0.1	330
	2004		0.08	3	0.1	330
PCB-1260	1998	0.04			0.1	330
	1999	0.04			0.1	330
	2000	0.02			0.1	330
	2001	0.01			0.1	330
	2003	0.02			0.1	330
	2004		0.1	4	0.1	330

[†]: Based upon data from 1998 to 2004 (see PCB_STAT.XLS).

Table 5. Matrix Spike Accuracy and Precision Data[†]

<i>Aroclor</i>	<i>Matrix</i>	<i>Spike</i>	<i>n</i>	<i>%Rec.</i>	<i>%RSD</i>	<i>LCL(%)</i>	<i>UCL(%)</i>
PCB-1016/1260	Water	0.5 µg/l	457	91.4	10.8	59.1	123.7
PCB-1016/1260	Soil	25.0 µg/kg	567	88.2	11.8	52.9	123.4

[†]: Based upon data from 01/02 to 12/03 (*see* PCB_STAT.XLS).Table 6. Surrogate Standard Recovery Ranges[†]

<i>Compound</i>	<i>Matrix</i>	<i>Spike</i>	<i>n</i>	<i>%Rec.</i>	<i>%RSD</i>	<i>LCL(%)</i>	<i>UCL(%)</i>
TCX (Tetrachloro-m-xylene)	Water	0.01 µg/l	845	85.7	16.8	35.4	136.0
	Soil	0.50 µg/kg	445	82.6	16.8	32.2	133.1
DCBP (Decachlorobiphenyl)	Water	0.01 µg/l	810	81.9	18.8	25.5	138.4
	Soil	0.50 µg/kg	393	81.8	18.8	25.4	138.2

[†]: Based upon sample data results from 01/02 to 12/03 (*see* PCB_STAT.XLS). These data include the effect of copper and sulfuric acid clean-up procedures, which are performed on all samples.

Table 7. Calibration Concentration Mixtures

<i>Aroclor</i>	<i>C₁(ppm)</i>	<i>C₂(ppm)</i>	<i>C₃(ppm)</i>	<i>C₄(ppm)</i>	<i>C₅(ppm)</i>
PCB-1016	0.1	0.3	0.5	0.8	1.0
PCB-1221	0.1	0.3	0.5	0.8	1.0
PCB-1232	0.1	0.3	0.5	0.8	1.0
PCB-1242	0.1	0.3	0.5	0.8	1.0
PCB-1248	0.1	0.3	0.5	0.8	1.0
PCB-1254	0.1	0.3	0.5	0.8	1.0
PCB-1260	0.1	0.3	0.5	0.8	1.0
PCB-1016/1260 [†]	0.1	0.3	0.5	0.8	1.0

[†]: The concentration for the 1016/1260 mixture is the concentration of each Aroclor.

Table 8. Standard Preparation for Calibration Mixtures

Revised: 9/18/01

Mixture Volume: 1000 ul
 Mixture Concentration: 100 mg/l
 Mixture Name: **PCB 1016/1260**

Compound/Mix	C(stock) mg/l	C(final) mg/l	V(stock) ul
PCB 1016	1000	100	100.00
PCB 1260	1000	100	100.00
Solvent - Hexane			800.00

Mixture Volume: 1000 ul
 Mixture Concentration: **0.5** mg/l

Compound/Mix	C(stock) mg/l	C(final) mg/l	V(stock) ul
PCB 1016/1260	100	0.5	5.00
TCX/DCBP	1.0	0.006	6.00
Solvent - Hexane			989.00

Mixture Volume: 1000 ul
 Mixture Concentration: **0.1** mg/l

Compound/Mix	C(stock) mg/l	C(final) mg/l	V(stock) ul
PCB 1016/1260	100	0.1	1.00
TCX/DCBP	1.0	0.002	2.00
Solvent - Hexane			997.00

Mixture Volume: 1000 ul
 Mixture Concentration: **0.8** mg/l

Compound/Mix	C(stock) mg/l	C(final) mg/l	V(stock) ul
PCB 1016/1260	100	0.8	8.00
TCX/DCBP	1.0	0.008	8.00
Solvent - Hexane			984.00

Mixture Volume: 1000 ul
 Mixture Concentration: **0.3** mg/l

Compound/Mix	C(stock) mg/l	C(final) mg/l	V(stock) ul
PCB 1016/1260	100	0.3	3.00
TCX/DCBP	1.0	0.004	4.00
Solvent - Hexane			993.00

Mixture Volume: 1000 ul
 Mixture Concentration: **1.0** mg/l

Compound/Mix	C(stock) mg/l	C(final) mg/l	V(stock) ul
PCB 1016/1260	100	1	10.00
TCX/DCBP	1.0	0.010	10.00
Solvent - Hexane			980.00

Table 9. Quality Control Items, Frequency and Corrective Action

QC Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (IC)	Prior to all analytical runs	Method-based	Examine the entire analytical system; some or all of the following: clip/replace column, heat detector, change injection septum, replace calibration standards, re-calibrate.
Continuing Calibration (CCV)	20 Samples / 12 hours	Method Based	Examine the entire analytical system; some or all of the following: clip/replace column, heat detector, change injection septum, replace calibration standards, re-calibrate; failure requires the re-analysis of all associated analytical runs.
LCS and MS	20 samples	Lab-based	A failed LCS should be re-extracted and re-analyzed. A failed MS requires no action provided that the LCS is acceptable. If additional sample exists, the samples associated with a failed LCS should be re-extracted and re-analyzed.
Duplicate or MSD	20 samples	n/a	Relative Percent Differences (RPDs) are computed and included in the QC report
Method Blank	20 samples	n/a	Method blank contamination is flagged on the analytical report for any identified target compound. Blanks indicative of contaminated extraction glassware should result in a thorough re-cleaning of the affected glassware. If the method blank contamination for a batch is atypical, the blank should be re-extracted and re-analyzed. If additional sample exists, the samples associated with a failed, re-extracted blank should also be re-extracted and re-analyzed.
Surrogate Standard	All samples	Lab-based	Adverse matrix effects on areas/recoveries are demonstrated either by screening the extract or re-analyzing the extract within a 12-hour QC batch. The resulting analytical report is flagged appropriately. If additional sample exists, the sample should be re-extracted prior to re-analysis if a matrix effect cannot be demonstrated.
Target Compound	All samples	Method-based	Target compounds beyond the calibration range are diluted and re-analyzed and/or flagged as estimated on the analytical report.

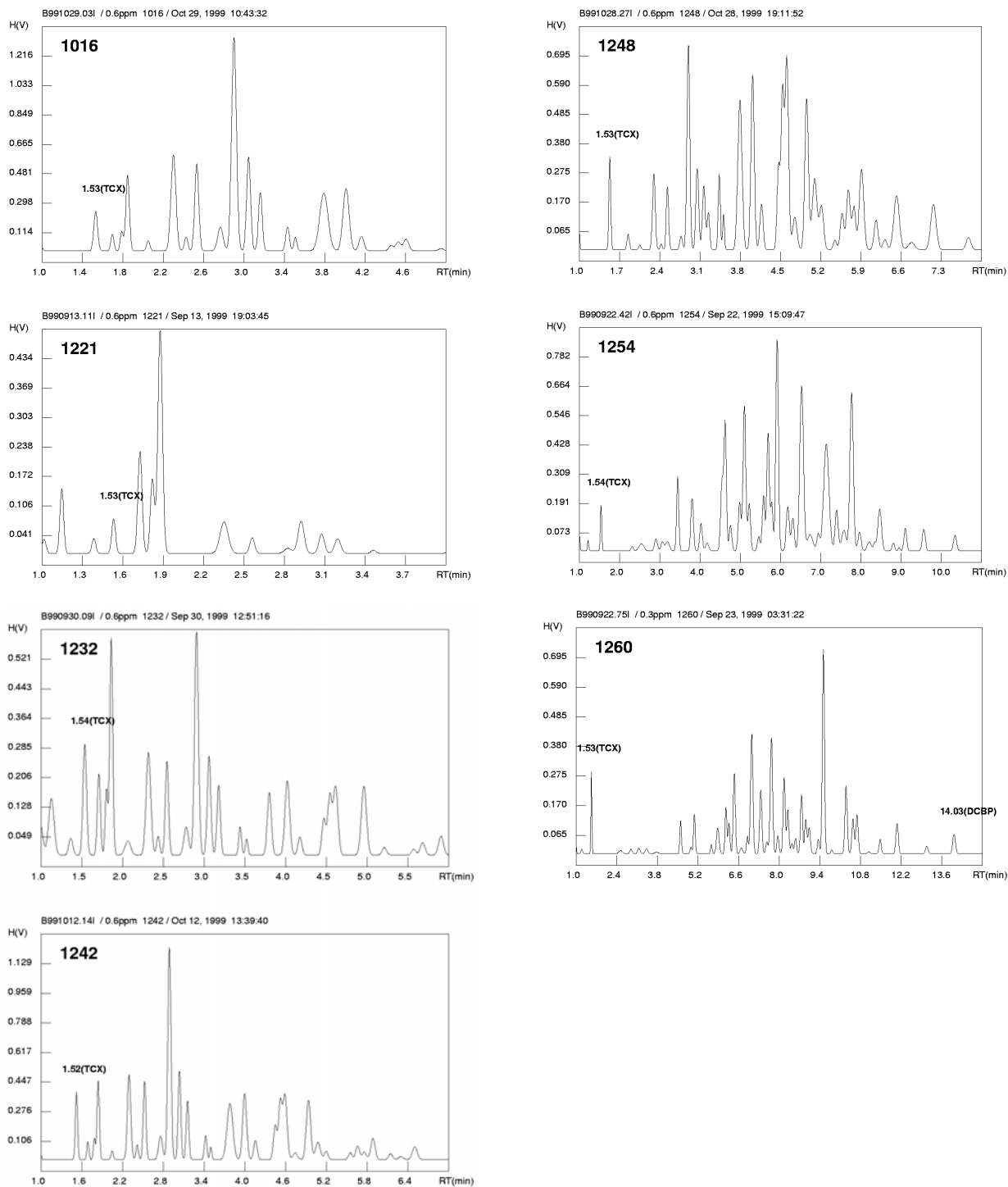


Figure 1. Example Aroclor chromatographic patterns from midpoint calibration standards for PCB 1016, 1221, 1232, 1242, 1248, 1254, and 1260 (column DB-5); based upon data from 09/99 to 10/99; see Table 2a for an enumeration of the retention times of the characteristic peaks.

10.0 APPROVAL AND ISSUE:

Analyst Date

Andy Ball, QA Officer Date

Maya V. Murshak, Technical Director Date

MICROWAVE ASSISTED ACID DIGESTION OF LIQUID SAMPLES AND EXTRACTS

1.0 SCOPE AND APPLICATION

- 1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis, by inductively coupled plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. The method referenced with in this SOP is SW-846 Method 3015A. This SOP is for use on all samples that do not require Ohio VAP certification.
- 1.2 Samples prepared by using nitric acid digestion are analyzed by ICP-MS for the following metals:

<u>Metal (Symbol)</u>	<u>CAS#:</u>
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Boron (B)	7440-42-8
Beryllium (Be)	7440-41-7
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-95-4
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Strontium (Sr)	7440-24-6
Thallium (Th)	7440-28-0
Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

2.0 SUMMARY OF METHOD

- 2.1 A representative 0.5 to 25 g/ml aqueous sample is digested in 1 ml of concentrated nitric acid in a polypropylene digestion vessel brought to a final volume of 50 ml and heated using microwave heating. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle prior to analysis.

3.0 INTERFERENCES

- 3.1 Addition of nitric acid to samples that contain organics, such as TCLP extracts, could result in a violent reaction and splattering (loss) of the sample, leading to loss of analytes and/or sample, which must be avoided. A smaller sample size can be used but the final water volume must be adjusted to approximately 10 ml prior to the heating stage.

4.0 APPARATUS AND MATERIALS

4.1 Microwave Digestion System CEM–Model MDS – 81D and MARSX-Model # 907600

4.1.1 The MDS-81D consists of a microwave drying system with an operator selectable power output of 0-600 watts in 1% increments, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon[®] coated cavity, exhaust tubing and standard screen rotating turntable, rotated at 6 rpm to insure uniform microwave heating.

4.1.2 The MARSX consists of a microwave drying system with an operator selectable power output of 0-1200 watts in, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon[®] coated cavity, exhaust tubing and standard rotating turntable, and self calibration features.

4.1.3 Microwave Digestion System Specifications:

MDS-81D		MARSX	
Power	600 Watts	Power	1200 Watts
Pressure	0 - 200 psi	Pressure	0 - 200 psi
Temperature	0 - 200°C	Temperature	0 - 200°C
Capacity	26 samples	Capacity	50 samples

4.2 Analytical balances, 510g capacity, minimum accuracy ± 0.001 g and 250g capacity, minimum accuracy ± 0.0001 g.

4.3 Filter funnel, glass or disposable polypropylene.

4.4 Glass-fiber filter paper, 0.45 μ m.

4.5 Membrane filters, 0.45 μ m.

4.6 Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

4.7 Disposable polypropylene vessels, 50 ml, compatible with centrifuge.

4.8 Plastic containers to support minimum of 200 ml.

4.9 Disposable Pasteur pipettes.

4.10 Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 μ l to 5,000 μ l.

4.11 Centrifuge (IEC Centra GP8)

5.0 REAGENTS

5.1 Trace metal grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, if applicable.

5.2 Deionized (DI) Water (Type I) is used which meets the specifications of the ASTM^[1] standard criteria.

5.3 Concentrated nitric acid, HNO₃, Trace Metal Grade. Acid purity is monitored by analysis of the laboratory reagent blank.

5.4 Standards added to digestion:

5.4.1 Spiking Solutions

^[1] 1985 Annual Book of ASTM Standards, Vol.11.01; "Standard Specification for Reagent Water"

- 5.4.1.1 Spiking solutions are prepared according to the Standard Prep Log. The formula, date source solutions, lot numbers, expiration date of stock standards, expiration date standard made, expiration and unique ID of any working standards used.
- 5.4.1.2 All standards are NIST traceable.
- 5.4.1.3 Multi-element standard solution WS1 (see standard prep book), containing Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mo, Mn, Ni, Se, Ag, Tl, Ti, V, Zn. This solution is made from stock NIST traceable standard and prepared according to the standard prep book.
 - 5.4.1.3.1 WS1 is used to make the QC Spiking Solution. The QC Spiking Solution is used to spike the LCS, MS, and MSD samples prior to digestion.
- 5.4.1.4 Multi-element standard solution HM (see standard prep book), containing 100 µg/ml each of Ca, K, Mg, Na. From this solution, 1.0 ml is added to the QC samples (*i.e.* MS/MSD samples), and 0.50 ml to the laboratory control sample (LCS), by weighing the amounts (1.0 g, 0.50 g) on the scale).

5.4.2 Internal Standards (After digestion):

- 5.4.2.1 Lithium 6, 1000 µg/ml stock solution.
- 5.4.2.2 Scandium, 1000 µg/ml stock solution.
- 5.4.2.3 Yttrium, 1000 µg/ml stock solution.
- 5.4.2.4 Rhodium, 1000 µg/ml stock solution.
- 5.4.2.5 Rhenium, 1000 µg/ml stock solution.
- 5.4.2.6 Internal Standard working solution (IS-WS): From the above stock solutions, 2.5 g of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO₃ and brought to a final volume of 1000 ml (by weight). The concentration in the flask will be 2.5 µg/ml. This represents the internal standards working solution from which 1 ml will be added to all samples (*i.e.* standards, samples, QC samples, blanks, etc.) prior to the analysis by the ICP/MS.

NOTE: The stock solutions are NIST traceable and provided with a certificate of analyses and MSDS sheets by the manufacturer.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 6.1 All samples are collected in appropriate containers. The samples are collected in HNO₃ pre-preserved plastic container and are acidified to pH of <2. (Approximately 125 ml volume).
- 6.2 Holding times for metals are 6 months from the date of sampling, with the exception of Mercury, which is not covered by this SOP.

7.0 PROCEDURE

- 7.1 Calibration of Microwave Equipment
 - 7.1.1 Microwaves are calibrated once a year according to the manufactures instructions.
- 7.2 All digestion vessels are disposable and are used only once, which allows for better sample control and prevents cross contamination.

CAUTION: -Toxic nitrogen oxide fumes may evolve, therefore all work must be performed in a properly operating ventilation system.
- Loss of sample through splattering inside the microwave system must be avoided. Physical observation is sufficient to determine if this is the case, therefore the batch of samples needs to be inspected at the end of the digestion cycle. If splattering has occurred, the samples are to be discarded, and a new batch is to be prepared.

7.3 Digestion using industrial Microwave.

- 7.3.1 A 0.5 to 25 ml/grams aliquot of a well shaken sample is transferred into the digestion vessel, sample volume is determined by sample matrix and sample history. The vessel is labeled with the sample number, which is also recorded on the preparation sheet.
- 7.3.2 With every batch of 20 analytical samples measure a volume of reagent water equal to the sample volume as described at 7.3.1 into a vessel labeled LRB. This represents the Laboratory Reagent Blank (LRB), which is carried through the entire digestion procedure, the same as an analytical sample.
- 7.3.3 With every batch of samples measure a volume of reagent water equal to the sample volume as described at 7.3.1 into a vessel labeled LCS. This represents the Laboratory Control Sample (LCS), which is carried through the entire digestion procedure, the same as an analytical sample.
- 7.3.4 For every 10 samples measure, in a similar manner, an amount equal to the parent sample of the sample designated for Matrix Spike (MS) and Matrix Spike duplicate (MSD) or duplicate (Dp).
- 7.3.4.1 Spiking for liquid samples is done by adding 0.5 ml of 5 ppm QC Spiking Solution.
- 7.3.5 Add 1 ml of concentrated nitric acid to each vessel, by using the bottle top dispenser in the hood.
- 7.3.6 For analysis of all metals except Ca, Mg, K and Na, add 0.5 ml of the QC Spiking Solution to the QC samples (LCS, MS/MSD). For Ca, Mg, K and Na, add 1.0 ml of the **HM** solution to the LCS, and 1.0 ml of the **HM** solution to the MS/MSD samples. The spike concentration and the Lot # of the stock solution used is recorded in the preparation log.

CAUTION: Addition of nitric acid to the non-aqueous (solvents) samples needs to be performed slowly, dropwise if possible in order to control the potential reaction. When the reaction has subsided, swirl the vessel lightly, dilute the sample to approximately 10 mL, and go to the next step.

- 7.3.7 Samples are slowly ramped in the microwave to 95±4 degrees Celsius over the course of a few minutes and maintained at this temperature for 30 minutes.
- 7.3.8 After the temperature program is completed, leave the vessels 5-10 minutes in the microwave, to cool down, and then move them into the hood. Add 1 ml of the Internal Standard working solution, using an Eppendorf automatic pipettor, and dilute to the 50 ml mark with DI Water into a calibrated digestion vessel (per lot).
- 7.3.9 If the digested sample contains particulate matter, which has the potential to clog the nebulizer, the sample needs to be centrifuged, allowed to settle, or filtered.
- 7.3.10 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this, however this can frequently be accomplished in a few hours. If it does not, centrifuge or filter the sample.
- 7.3.11 Centrifugation: Centrifugation at 4500 rpm for 3 minutes is usually sufficient to clear the supernatant.
 - 7.3.11.1 Filtering: The filtering apparatus (flask and funnel) must be thoroughly rinsed with a 10% v/v nitric acid solution and copious amounts of DI Water. Filter the sample through a 0.45 µm filter paper and transfer the liquid to a new vessel. Glass fiber

filters are acceptable for all metals except Zn and Ba, for which membrane filters are required, due to the presence of these elements in the glass fiber filters.

7.3.12 Calculate the dilution factor (DF) by the formula:

$$DF = \frac{\text{Final Volume (50)}}{\text{Sample amount}}$$

7.3.13 This dilution factor is recorded in the sample preparation log, and is to be used in the determination of the final result by the ICP/MS.

8.0 QUALITY CONTROL

- 8.1 For each analytical batch of 20 samples processed, one laboratory reagent blank (LRB) must be carried throughout the entire sample preparation and analytical process. The LRB will be used for determining if the samples are being contaminated during preparation or from reagents.
- 8.2 For each analytical batch of 20 samples processed, one laboratory control sample (LCS) must be carried throughout the entire sample preparation and analytical process. The LCS will be used for determining the performance of the method for that particular batch.
- 8.3 Spiked samples (MS) must be employed to determine accuracy. A spiked sample must be included with each group of 10 samples processed.
- 8.4 Duplicate (Dp) samples or Matrix Spike Duplicate (MSD) must be processed for every ten samples. A duplicate sample is a real sample brought through the whole sample preparation and analytical process.
- 8.5 For each analytical batch of 20 sample processed the laboratory must perform a dilution test. The dilution test is performed by taking 10 ml of a parent sample after digestion and adding 0.8 ml of acid and 0.8 ml of internal standard and bring to a final volume of 50 ml. The dilution test is used to identify matrix interference and is not applicable if the measured concentration is less than 100 time the MDL for each measured analyte.

9.0 WASTE DISPOSAL

9.1 Samples

- 9.1.1 All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory waste water.
- 9.1.2 As a "small generator" of metals, Merit laboratories has been approved for this type of disposal from the local government.

9.2 Acid bottles

- 9.2.1 Acid bottles are rinsed out and neutralized with baking soda before being disposed of with the normal laboratory waste.

10.0 DOCUMENTATION

- 10.1 All pertinent information is entered into a digestion logbook. The digestion log sheet has to contain the following information on the header/table:
 - Date.
 - Analyst initials.
 - Method reference.
 - Sample #.
 - Sample weight or volume.
 - MS/MSD/LCS spike concentration.
 - Total solids (if applicable)

- Acid Lot #
- Spike Lot #
- Dilution Factor
- Prep batch
- Final volume of sample
- Remarks
-

11.0 METHOD PERFORMANCE

- 11.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

12.0 REFERENCES

- 12.1 Horlick, G., et al., Spectrochim. Acta 40B, 1555 (1985).
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- 12.3 Tan, S.H., and Horlick, G., Appl. Spectrosc. 40, 445 (1986).
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- 12.5 Holden, N.E., "Table of the Isotopes," in Lide, D.R., Ed., CRC Handbook of Chemistry and Physics, 74th Ed., CRC press, Boca Raton, FL, 1993.
- 12.6 Hinnners, T.A., Heithmar, E., Rissmann, E., and Smith, D., Winter Conference on Plasma Spectrochemistry, Abstract THP18; p. 237, San Diego, CA (1994).
- 12.7 Lichte, F.E., et al., Anal. Chem. 59, 1150 (1987).
- 12.8 Evans E.H., and Ebdon, L., J. Anal. At. Spectrom. 4, 299 (1989).
- 12.9 Beauchemin, D., et al., Spectrochim. Acta 42B, 467 (1987).
- 12.10 Houk, R.S., Anal. Chem. 58, 97A (1986).
- 12.11 Thompson, J.J., and Houk, R.S., Appl. Spectrosc. 41, 801 (1987).
- 12.12 SW-846, Method 6020 Revision 0, 1994.
- 12.13 Method 200.8, Revision 5.4, 1998.
- 12.14 SW-846, Method 6020A Revision 1, 2007
- 12.15 SW-846, Method 8000C Revision 3, 2003
- 12.16 SW-846, Method 3015

13.0 SAFETY

- 13.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 13.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit.
- 13.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.
- 13.4 Specific attention be paid (but not limited) to
- 13.4.1 Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.
 - 13.4.2 Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.
 - 13.4.3 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.
 - 13.4.4 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

14.0 APPROVAL & ISSUE:

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

Analyst	Date
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Andy Ball, QA/QC Officer	Date
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Maya V. Murshak, Technical Director	Date
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SOP #043550B: ULTRASONIC EXTRACTION FOR BNAs/PNAs/HERBICIDES
USING METHOD 3550B

Revision: 5
Date: 03/03/06

Location: Extraction Laboratory
Semi-volatiles GC/MS Laboratory
QA Officer's Files

These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods.

1.0 SCOPE AND APPLICATION

- 1.1 This method is used for extracting nonvolatile and semivolatile base/neutral/acid (BNA), polynuclear aromatic hydrocarbon (PNA) and herbicides organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

2.0 SUMMARY OF METHOD

- 2.1 For most of samples, 2g - 30g sample (depending on the matrix; 30g is typical for a soil) is mixed with anhydrous sodium sulfate to form a free-flowing solid. Extract with methylene chloride using ultrasound. For herbicides samples, acidified sodium sulfate is used instead.
- 2.2 The extract is separated from the sample and concentrated.
- 2.3 Clean glassware and matrix cleanup procedures are used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

- 3.1 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate.
- 3.2 Degradation of PCBs, as well as more complex matrix (i.e. oil, tar, sulfur, etc.) can interfere with the "clarity" of the chromatograms.

4.0 APPARATUS AND MATERIALS

- 4.1 Apparatus for grinding dry waste samples
- 4.2 Ultrasonic device - Branson Sonifier, Model 450
- 4.3 Ultrasonic Disrupter - power wattage of 300 watts, with pulsing.
- 4.3.1 3/4" horn
- 4.3.2 Sonabox - (Ultrasonics #432B)
- 4.4 Apparatus for percent dry weight
- 4.4.1 Drying oven (105°C - 120°C)
- 4.4.2 Dessicator
- 4.4.3 Crucibles - disposable aluminum
- 4.4.4 Glass pipettes - 1ml, disposable
- 4.4.5 Beakers - 250ml
- 4.4.6 Filter paper - Whittman No. 41
- 4.5 Zymark Evaporation Station
- 4.6 Evaporation tubes
- 4.7 Water bath - Heated, capable of temperature control ($\pm 5^{\circ}\text{C}$).
- 4.8 Balance - Top-loading, capable of accurately weighing to the nearest 0.01 g.
- 4.9 Vials - 4 ml, with polytetrafluoroethylene (PTFE)-lined screw caps.
- 4.10 Glass scintillation vials - 20-mL, with PTFE-lined screw caps.
- 4.11 Tongue depressors, disposable
- 4.12 Beakers - 250ml
- 4.13 Glass funnel
- 4.14 Filter paper, coarse grade
- 4.15 Adhesive labels
- 4.16 Syringe - 5-mL NIST certified
- 4.17 250mL Erlenmeyer flasks

5.0 REAGENTS

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Note: Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

- 5.1 Sodium sulfate (granular, anhydrous), Na_2SO_4 .
- 5.2 Extraction - All solvents must be pesticide quality or equivalent
 - 5.2.1 Methylene Chloride, CH_2Cl_2 .
 - 5.2.2 Hexane, C_6H_{14} .
 - 5.2.3 Acetone, $\text{C}_3\text{H}_6\text{O}$.
- 5.3 Surrogate and matrix spiking solutions are prepared as listed in Table 1. The detailed list of compounds for each stock mixture is given in §9.
- 5.4 High purity Ether

6.0 SAMPLE CONTAINERS AND STORAGE

- 6.1 All samples for the analysis of BNAs/PNAs/Herbicides are stored in small glass containers only.
- 6.2 Approximately 2 to 30 g (depending on the matrix) of sample is needed for extraction.
- 6.3 Refrigerate at 4°C.
- 6.4 Holding Time for solid samples is 14 days to extraction and 40 days after extraction.

7.0 GLASSWARE CLEANING

Note: All glassware must be immaculate. Glassware should be cleaned as soon as possible after the extraction. A quick reference guide is posted in the extraction laboratory.

- 7.1 Immediately after use rinse glassware with the last solvent used in it. Drain it into a bottle labeled "Wash Solvent."
- 7.2 Wash well with hot water and laboratory detergent by hand.
- 7.3 Rinse three times with hot tap water followed by three times with DI water.
- 7.4 Place in dishwasher.
- 7.5 Rinse with acetone.
- 7.6 Rinse with hexane.

8.0 PROCEDURE^[1]

- 8.1 The extraction device has a minimum of 300 watts of power and is equipped with ¾" size disrupter horns.
 - 8.1.1 The horn is maintained, by inspection of the horn tip for excessive wear that would be seen as "cavities" on the bottom of the instrument.
 - 8.1.2 Samples are prepared by thorough mixing with sodium sulfate so that it forms a free-flowing solid prior to the addition of the solvent.
 - 8.1.3 Three extractions are performed with 60ml of Methylene Chloride solvent for 3 minutes each. For herbicides, use ether instead of methylene chloride.
 - 8.1.4 Extraction is performed in the specified pulse mode, and the horn tip is positioned just below the surface of the solvent yet above the sample.
 - 8.1.5 Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. Observe such mixing at some point during the extraction process to insure that the placement of the horn is correct.
- 8.2 Sample handling
 - 8.2.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.
 - 8.2.2 Waste samples - Samples consisting of multiple phases are separated into two phases. Per client request one or the other phase is extracted. If both phases need to be extracted, two separate extractions are performed.

¹ Reference for this procedure is SW-846, Revision 3, December 1996 Method 3550B, Ultrasonic Extraction

SOP #043550B: ULTRASONIC EXTRACTION FOR BNAs/PNAs/HERBICIDES
USING METHOD 3550B

Revision: 5
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- 8.2.3 Dry waste samples amenable to grinding - Grind or drill the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Minimum of 10g of sample should pass through the sieve.
- 8.2.4 Gummy, fibrous, or oily materials not amenable to grinding are cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction.
- 8.3 Extraction method
- 8.3.1 Weigh approximately 2-30 g of sample (depending on the matrix) into a 250-ml beaker. Record the weight to the nearest 0.1 g.
- 8.3.1.1 The default weight used is 30g for a soil sample.
- 8.3.1.2 If the sample is a solvent or an oil matrix, approximately 2g of the neat sample is put into a 4ml screw cap vial and given to the GC/MS analyst. No extraction is performed due to the exceptionally high chromatographic response of these sample types. These samples are diluted by a factor of 400:1 and analyzed directly (see Table 8, SOP: 8270B.901.doc). The relative response of this base dilution may result in a final analysis of the sample at a higher or lower net dilution.
- 8.3.2 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using disposable tongue depressors. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.
- 8.3.3 a) For BNA extraction: Add 1.0 ml of the BNA surrogate standard solution to all samples, spiked samples, QC samples, and blanks (see Table 1).
b) For PNA extraction: Add 1.0 ml of the PNA surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 1).
c) For DRO extraction: Add 1.0 ml of the DRO surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 1).
d) For herbicides extraction: Add 1.0 ml of the HERB surrogate standard solution to all samples. Spiked samples, QC samples, and blanks (see Table 1).
- 8.3.4 For the sample in each batch selected for spiking (*i.e.* LCS, MS, MSD), add 1.0 ml of the matrix spiking solution (BNA, PNA, DRO, or HERB as appropriate, see Table 1).
- 8.3.5 Place the bottom surface of the tip of the 3/4 inch disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer.
- 8.3.6 Extract ultrasonically for 3 minutes, with output control knob set at 6 and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time).
- 8.3.7 Decant through a conical gravity filter (Whatman No. 41 filter paper) and sodium sulfate to catch any excess water into an evaporation tube. For herbicides, decant into a 250mL Erlenmeyer flask with 10-15g acidified sodium sulfate.
- 8.3.8 Repeat the extraction with two additional 60 ml portions of methylene chloride. Pour off the solvent after the ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample onto the filter with extraction solvent.
- 8.3.9 For herbicides, let the 250 mL Erlenmeyer flask stand with occasional swirling for two hours. Transfer the extract to an evaporation tube.
- 8.4 Evaporation method
- 8.4.1 Place the concentrator tube in the TurboVap Evaporation Station, that has the water bath at 42±2°C, 21 psi, until the extract reaches a 1 ml final volume.
- 8.4.2 Transfer the sample extract to a 4 ml pre-calibrated vial. Adjust to 1 ml final volume.
- 8.4.3 For herbicides follow the diazomethane methylation procedure outlined in the diazomethane generation SOP.

9.0 QUALITY CONTROL

- 9.1 Samples are extracted in batches of 20 samples or less. For every batch there should be a Blank, LCS, MS, and MSD/DUP depending on the clients request. All the reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples. In

SOP #043550B: ULTRASONIC EXTRACTION FOR BNAs/PNAs/HERBICIDES
USING METHOD 3550B

Revision: 5
Date: 03/03/06

case of the client not providing the necessary sample volume to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.

- 9.2 The B/N surrogate standard must contain the following compounds: Nitrobenzene-d5, 5,000 ug/ml (CAS 4165-60-0), 2-fluorobiphenyl, 5,000 ug/ml (CAS 321-60-8), p-terphenyl-d14, 5,000 ug/ml (CAS 1718-51-0). Cat. No. 31086, RESTEK (800-356-1688). The Acid surrogate standard must contain the following compounds: 2-fluorophenol, 10,000 ug/ml (CAS 367-12-4), Phenol-d6, 10,000 ug/ml (CAS 13127-88-3), 2,4,6-tribromophenol, 10,000 ug/ml (CAS 118-79-6). Cat. No. 31087, RESTEK (800-356-1688). The concentrations listed are those in the stock spiking solutions. [the Acid surrogate standard is N/A for the PNA method.] The surrogate standard is prepared according to Table 1.
- 9.3 The B/N MS/MSD and LCS spikes will contain the following compounds; Acenaphthene, 5,000 ug/ml (CAS 83-32-9), 1,4-dichlorobenzene, 5,000 ug/ml (CAS 106-46-7), 2,4-dinitrotoluene, 5,000 ug/ml (CAS 121-14-2), n-nitroso-di-n-propylamine, 5,000 ug/ml (CAS 621-64-7), Pyrene, 5,000 ug/ml (CAS 129-00-0), 1,2,4-trichlorobenzene, 5,000 ug/ml (CAS 120-82-1). Cat. No. 31074, RESTEK (800-356-1688). The Acid MS/MSD and LCS spikes will contain the following compounds: 4-chloro-3-methylphenol, 10,000 ug/ml (CAS 59-50-7), 2-chlorophenol, 10,000 ug/ml (CAS 95-57-8), 4-nitrophenol, 10,000 ug/ml (CAS 100-02-7), pentachlorophenol, 10,000 ug/ml (CAS 87-86-5), phenol, 10,000 ug/ml (CAS 108-95-2). Cat. No. 31061/31071, RESTEK (800-356-1688). The concentrations listed are those in the stock spiking solutions. MS/MSD spike should be prepared at a concentration at or below the medium level of the BNA curve. The MS/MSD and LCS standards are prepared according to Table 1.
- 9.4 The PNA MS/MSD and LCS spikes will contain the following compounds; Naphthalene, 2,000 ug/ml, 2-Methylnaphthalene, 2,250 ug/ml, Acenaphthylene, 2,000 ug/ml, Acenaphthene, 2,000 ug/ml, Flourene, 2,000 ug/ml, Phenanthrene, 2,000 ug/ml, Anthracene, 2,000 ug/ml, Flouranthene, 2,000 ug/ml, Pyrene, 2,000 ug/ml, Benzo (a) anthracene, 2,000 ug/ml, Chrysene, 2,000 ug/ml, Benzo (b) flouranthene, 2,000 ug/ml, Benzo (k) flouranthene, 2,000 ug/ml, Benzo (a) pyrene, 2,000 ug/ml, Indeno (1,2,3-cd) pyrene, 2,000 ug/ml, Dibenzo (ah) anthracene, 2,000 ug/ml, Benzo(ghi) perylene, 2,000 ug/ml. The concentrations listed are those in the stock spiking solutions. MS/MSD spike should be prepared at a concentration at or below the medium level of the PNA curve. The MS/MSD and LCS standards are prepared according to Table 1.
- 9.5 The DRO MS/MSD and LCS spikes contains neat diesel fuel diluted to a concentration appropriate for the sensitivity of the GC/MS (1000 mg/L). The MS/MSD and LCS standards are prepared according to Table 1.
- 9.6 New lot blanks are analyzed to insure the purity of the materials and reagents.

Note: The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced.

10.0 DOCUMENTATION

- 10.1 All pertinent information is entered into an extraction logbook (See Table 1). The extraction log sheet has to contain the following information on the header/table:

- Date
- ANALYSTS INITIALS
- Method
- Surrogate/MS/MSD/LCS standard unique traceability ID
- Methylene Chloride #
- Sample #
- Matrix
- Sample weight
- Solvent ID & Volume (ml)
- Final extract volume

SOP #043550B: ULTRASONIC EXTRACTION FOR BNAs/PNAs/HERBICIDES
USING METHOD 3550B

Revision: 5
Date: 03/03/06

- Surrogate standard spike volume
- MS spike volume

11.0 REFERENCES

11.1 Method 3550A SW

12.0 APPROVAL & ISSUE

12.1 The following personnel have read, accepted and approved this standard operating practice:

Analyst

Date

Andy Ball, QA Officer

Date

Maya V. Murshak, Technical Director

Date

13.0 Tables

Table 1. Surrogate and Spike Preparation for use in Extraction

BNA Surrogate:

For 100 ml total solution at 100 mg/L:
97 ml of Acetone
1 ml of 10,000 mg/L Acids surrogate
2 ml of 5,000 mg/L B/N surrogate

BNA MS Spike:

For 20 ml total solution at 50 mg/L:
19.7 ml of Acetone
100 ul of 10,000 mg/L Acids spike
200 ul of 5,000 mg/L B/N spike

PNA/DRO Surrogate:

For 100 ml total solution at 100 mg/L:
98 ml of Acetone
2 ml of 5,000 mg/L B/N surrogate

PNA MS Spike:

For 20 ml total solution at 50 mg/L:
19.1 ml of Acetone
500 ul of 2,000 mg/L PNA stock
444 ul of 2250 mg/L 2-Methylnaphthalene stock

DRO MS Spike:

For 20 ml total solution at 1000 mg/L;
20.0 ml of Acetone
20.0 mg of neat Diesel Fuel (gravimetric preparation)

SOP #043510C: SEPARATORY FUNNEL EXTRACTION FOR BNAs/PNAs/TCLP/HERBICIDES
BY METHOD 3510C

Revision: 6
Date: 03/03/06

Location: Extraction Laboratory
GC/ECD
GC/MS Laboratory
QA Director's Office Files

These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods.

1.0 SCOPE AND APPLICATION

1.1 This method is used for extracting nonvolatile and semivolatile base/neutral/acid (BNA) and polynuclear aromatic hydrocarbon (PNA) organic compounds from aqueous samples. This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures. The BNA following method is congruent with TCLP and TTO procedures in their entirety and may also be used with PNA and Herbicide methods (with the omission or addition of appropriate steps).

2.0 SUMMARY OF METHOD

- 2.1 A measured volume of sample, usually 1 liter, is extracted with methylene chloride using a separatory funnel.
- 2.2 The extract is concentrated.
- 2.3 Clean glassware is used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

3.1 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate, phthalate esters may exchange, and phenols may react to form tannates.

4.0 APPARATUS AND MATERIALS

- 4.1 Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.
- 4.2 Evaporation tubes, 250-ml volume, Zymark with end point of 0.5-ml.
- 4.3 Zymark Turbo Vap II Concentration Station with temperature control water bath.
- 4.4 Vials - 4-ml, glass with PTFE-lined screw caps or crimp tops.
- 4.5 pH indicator paper - pH range including the desired extraction pH.
- 4.6 Glass beakers, 250-ml.
- 4.7 Glass funnel
- 4.8 Filter paper, coarse grade
- 4.9 Adhesive labels
- 4.10 Syringe - 5-mL NIST certified
- 4.11 Graduated cylinder - 1-liter
- 4.12 250 mL Erlenmeyer flasks

5.0 REAGENTS

Note: Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

- 5.1 Reagent water
- 5.2 Sodium sulfate (granular, anhydrous), Na₂SO₄.
- 5.3 Sulfuric acid, concentrated, as well as solution (1:1 v/v), H₂SO₄. Slowly add 50-ml of H₂SO₄ to 50-ml of DI water.
- 5.4 Sodium Hydroxide solution (1:1 v/v), NaOH. Slowly add 46 ml of DI water to 2-g of NaOH crystals.
- 5.5 Extraction/exchange solvents

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- 5.5.1 Methylene chloride, CH_2Cl_2 , boiling point 49°C .
- 5.5.2 Hexane, C_6H_{14} .
- 5.5.3 Acetone, $\text{C}_3\text{H}_6\text{O}$.
- 5.6 Surrogate and matrix spiking solutions are prepared as listed in Table 1. The detailed list of compounds for each stock mixture is given in §9.
- 5.7 High purity Ether

6.0 SAMPLE CONTAINERS AND STORAGE

- 6.1 All samples for the analysis of BNAs should be stored in Amber glass containers only.
- 6.2 Approximately 1-L volume of sample is needed for extraction.
- 6.3 Refrigerate at 4°C .
- 6.4 The holding time for samples is 7 days until extraction and 40 days thereafter.

Note: If samples contain significantly less volume than 1L, QA & client need to be notified. Higher detection limits will be applied to low volume extracts.

7.0 GLASSWARE CLEANING

- 7.1 Immediately after use, rinse glassware with the last solvent used in it. Drain it into a bottle labeled "Wash Solvent"
- 7.2 Wash well with hot water and laboratory detergent by hand.
- 7.3 Rinse three times with hot tap water followed by three times with DI water.
- 7.4 Place in dishwasher.
- 7.5 Rinse with acetone.
- 7.6 Rinse with hexane.

Note: All glassware must be immaculate. Glassware should be cleaned as soon as possible after the extraction. A quick reference guide is posted in the extraction laboratory. If the glassware is extremely dirty or has not been treated in more than a week, coat and soak it with concentrated H_2SO_4 preferably with Nonchromix added. Then rinse with tap water and follow the cleaning procedure above.

8.0 PROCEDURE^[1]

- 8.1 Mark the level of sample on the outside of the bottle. Pour the sample into the 2-liter separatory funnel.
- 8.2 For all samples, spikes, and blanks, pipette 1.0-ml of the appropriate surrogate spiking solution (see Table 1 and §9.2) into the funnel and swirl.
 - 8.2.1 For matrix spike samples (including the LCS), add 1ml surrogate and 1-ml matrix spike standard (see Table 1 and §9.3). These volumes are appropriate for BNA, PNA, herbicide and DRO samples.
 - 8.2.2 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to a pH < 2 using H_2SO_4 .
- 8.3 Add 10-ml of Acetone into the separatory funnel and swirl the sample (N/A for herbicides and PNAs).
- 8.4 Add 35-ml (for PNA's and phenols), or 30 ml (for BNA/TCLP) of methylene chloride into the sample bottle to rinse it and transfer this rinse solvent to the separatory funnel (for herbicides, use ether instead of methylene chloride).
- 8.5 Seal the separatory funnel and shake vigorously for 3 minutes on a horizontal placement at motor speed 70 in accordance with Table 2 shake program. Initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors. Allow the organic layer to separate from the water phase for 1 to 10 minutes, depending on the matrix of the sample.

¹ Reference for this procedure is SW-846, Revision 3, December 1996 Method 3510C, Separatory Funnel Extraction.

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- 8.5.1 *Note: If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.*
- 8.6 Drain the extract through a filter filled with approximately 10g of Na₂SO₄ into a 250-ml glass Zymark evaporation tube. (For herbicides, drain the extract into a 250-mL Erlenmeyer flask with approximately 10-15g acidified sulfate in the bottom.)
- 8.7 Add 35ml (for PNA/phenols), or 35 ml (for BNA/TCLP) methylene chloride to the separatory funnel. Seal and shake the separatory funnel vigorously for 1 minute on a horizontal placement at motor speed 74. Vent the funnel and continue for 2 minutes in accordance with Table 2 shake program. Initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors. Allow the organic layer to separate from the water phase for 1 to 10 minutes, depending on the matrix of the sample. (For herbicides, use ether in place of methylene chloride.)
- 8.8 Repeat step 9.7 twice more with 35ml, or appropriate volume, methylene chloride each in accordance with Table 2 shake program [Repeat only once with PNA or DRO methods]. (For herbicides, use ether in place of methylene chloride and skip to step 8.12.)
- 8.8.1 *Note: Samples requiring PNA and/or DRO analysis may be extracted in an analytical batch for BNAs, using the additional procedural steps and surrogate compounds, without loss of generality.*
- 8.9 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to a pH > 12 using NaOH [N/A for PNAs or DROs].
- 8.10 Repeat step 9.7 two times at two minutes each in accordance with Table 2 shake program [N/A for PNAs].
- 8.11 Rinse the funnel and Na₂SO₄ with 20-ml Methylene chloride into the collected sample.
- 8.12 For herbicides only, let the extract stand in the Erlenmeyer flask with occasional swirling for two hours. Transfer to evaporation tube.
- 8.1 After all of the extract solvent has been collected, place the evaporation tube into the Turbo Vap II evaporation station, with the bath water at 42°C +/- 2°C and 21 psi. Allow the sample to evaporate down to 1ml methylene chloride or until the evaporation station signals completion. Use nitrogen to blow down the sample to make sure that it does not spill out.
- 8.14 Transfer the final volume into a pre-calibrated 4-ml glass vial, rinse the evaporation tube with clean methylene chloride and bring to 1-ml. If the final volume is over 1ml, use nitrogen gas or a special airline to evaporate to the 1-ml mark
- 8.15 Find the original volume of the sample by pouring tap water into the sample container to the mark. Pour the water into a 1000 ml graduated cylinder, and record the volume in the extraction logbook and label.
- 8.16 For final herbicide extracts, follow diazomethane methylation procedures as explained in the SOP for its method.

9.0 QUALITY CONTROL

- 9.1 Samples are extracted in batches of 20 samples or less. For every batch there should be a Blank, LCS, MS, and MSD/DUP depending on the client's request. All the reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample volume to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.
- 9.2 The B/N surrogate standard must contain the following compounds: Nitrobenzene-d5, 5,000 ug/ml (CAS 4165-60-0), 2-fluorobiphenyl, 5,000 ug/ml (CAS 321-60-8), p-terphenyl-d14, 5,000 ug/ml (CAS 1718-51-0). Cat. No. 31086, RESTEK (800-356-1688). The Acid surrogate standard must contain the following compounds: 2-fluorophenol, 10,000 ug/ml (CAS 367-12-4), Phenol-d6, 10,000 ug/ml (CAS 13127-88-3), 2,4,6-tribromophenol, 10,000 ug/ml (CAS 118-79-6). Cat. No. 31087, RESTEK (800-356-1688). The concentrations listed are those in the stock spiking solutions. The Acid surrogate standard is N/A for the PNA and DRO methods. The surrogate standard is prepared according to Table 1.

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- 9.3 The B/N MS/MSD and LCS spikes will contain the following compounds; Acenaphthene, 5,000 ug/ml (CAS 83-32-9), 1,4-dichlorobenzene, 5,000 ug/ml (CAS 106-46-7), 2,4-dinitrotoluene, 5,000 ug/ml (CAS 121-14-2), n-nitroso-di-n-propylamine, 5,000 ug/ml (CAS 621-64-7), Pyrene, 5,000 ug/ml (CAS 129-00-0), 1,2,4-trichlorobenzene, 5,000 ug/ml (CAS 120-82-1). Cat. No. 31074, RESTEK (800-356-1688). The Acid MS/MSD and LCS spikes will contain the following compounds: 4-chloro-3-methylphenol, 10,000 ug/ml (CAS 59-50-7), 2-chlorophenol, 10,000 ug/ml (CAS 95-57-8), 4-nitrophenol, 10,000 ug/ml (CAS 100-02-7), pentachlorophenol, 10,000 ug/ml (CAS 87-86-5), phenol, 10,000 ug/ml (CAS 108-95-2). Cat. No. 31061/31071, RESTEK (800-356-1688). The concentrations listed are those in the stock spiking solutions. MS/MSD spike should be prepared at a concentration at or below the medium level of the BNA curve. The MS/MSD and LCS standards are prepared according to Table 1.
- 9.4 The PNA MS/MSD and LCS spikes will contain the following compounds; Naphthalene, 2,000 ug/ml, 2-Methylnaphthalene, 2,250 ug/ml, Acenaphthylene, 2,000 ug/ml, Acenaphthene, 2,000 ug/ml, Flourene, 2,000 ug/ml, Phenanthrene, 2,000 ug/ml, Anthracene, 2,000 ug/ml, Flouranthene, 2,000 ug/ml, Pyrene, 2,000 ug/ml, Benzo (a) anthracene, 2,000 ug/ml, Chrysene, 2,000 ug/ml, Benzo (b) flouranthene, 2,000 ug/ml, Benzo (k) flouranthene, 2,000 ug/ml, Benzo (a) pyrene, 2,000 ug/ml, Indeno (1,2,3-cd) pyrene, 2,000 ug/ml, Dibenzo (ah) anthracene, 2,000 ug/ml, Benzo(ghi) perylene, 2,000 ug/ml. The concentrations listed are those in the stock spiking solutions. MS/MSD spike should be prepared at a concentration at or below the medium level of the PNA curve. The MS/MSD and LCS standards are prepared according to Table 1.
- 9.5 The DRO MS/MSD and LCS spikes contains neat diesel fuel diluted to a concentration appropriate for the sensitivity of the GC/MS (1000 mg/L). The MS/MSD and LCS standards are prepared according to Table 1.
- 9.6 New lot blanks are analyzed to insure the purity of the materials and reagents.
- 9.6.1 *Note: The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced.*

10.0 DOCUMENTATION

- 10.1 All pertinent information is entered into an extraction logbook. The extraction log sheet has to contain the following information on the header/table:
- Date
 - ANALYSTS INITIALS
 - Method
 - Surrogate/MS/MSD/LCS standard unique traceability ID
 - Methylene Chloride Lot #
 - Sample I.D. #
 - Matrix
 - Sample volume
 - Solvent ID & Volume (ml)
 - Final extract volume
 - Surrogate standard spike volume
 - MS spike volume

11.0 REFERENCES

11.1 Method 3510C SW

12.0 APPROVAL & ISSUE:

- 12.1 The following personnel have read, accepted and approved this standard operating practice.

SOP #043510C: SEPARATORY FUNNEL EXTRACTION FOR BNAs/PNAs/TCLP/HERBICIDES
BY METHOD 3510C

Revision: 6
Date: 03/03/06

Analyst	Date
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Andrew Ball, QA Officer	Date
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Maya V. Murshak, Technical Director	Date
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12.0 TABLES

Table 1. Surrogate and Spike Preparation for use in Extraction

BNA Surrogate:

For 100 ml total solution at 100 mg/L;
97 ml of Acetone
1 ml of 10,000 mg/L Acids surrogate
2 ml of 5,000 mg/L B/N surrogate

BNA MS Spike:

For 20 ml total solution at 50 mg/L;
19.7 ml of Acetone
100 ul of 10,000 mg/L Acids spike
200 ul of 5,000 mg/L B/N spike

PNA/DRO Surrogate:

For 100 ml total solution at 100 mg/L;
98 ml of Acetone
2 ml of 5,000 mg/L B/N surrogate

PNA MS Spike:

For 20 ml total solution at 50 mg/L;
19.1 ml of Acetone
500 ul of 2,000 mg/L PNA stock
444 ul of 2,250 mg/L 2-Methylnaphthalene stock

DRO MS Spike:

For 20 ml total solution at 1000 mg/L;
20.0 ml of Acetone
20.0 mg of neat Diesel Fuel (gravimetric preparation)

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Table 2. Automated Extraction Funnel Shaking Procedure.

Stage	Solvent Volume	pH	Funnel Position	Shaker Time	Shaker Intensity	BNA Extraction	PNA/DRO Extraction
1a	30 ml	<2	vertical/open	1 min.	68	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
1b			horizontal/closed	2 min.	70	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
2a	30 ml	<2	horizontal/closed	1 min.	74	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
2b			horizontal/closed	2 min.	74	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
3	30 ml	<2	horizontal/closed	3 min.	74	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
4	30 ml	<2	horizontal/closed	3 min.	74	<input checked="" type="checkbox"/>	<input type="checkbox"/>
5	30 ml	>12	horizontal/closed	3 min.	74	<input checked="" type="checkbox"/>	<input type="checkbox"/>
6	30 ml	>12	horizontal/closed	3 min.	74	<input checked="" type="checkbox"/>	<input type="checkbox"/>

- Notes:*
- (1) *Funnel Position* indicates whether the funnel is horizontally or vertically situated in the automatic shaker and whether the stopcock is open or closed.
 - (2) *Shaker Time* is the timer setting on the shaker unit. The funnel is vented at the end of every time interval (*i.e.* 1, 2, or 3 minutes).
 - (3) *Shaker Intensity* is the dial setting on the automatic shaker unit. A higher number indicates a more vigorous shake.
 - (4) *BNA/PNA/DRO Extraction* indicates whether the extraction stage is appropriate for the given class of analytes.

METHOD 3550B PCBs/PESTICIDES

Location: Extraction Laboratory; GC/ECD Laboratory

These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods.

1.0 SCOPE AND APPLICATION

- 1.1 This method is used for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent. The extracts are cleaned up prior to analysis.

2.0 SUMMARY OF METHOD

- 2.1 For most samples, 1g - 30g of sample (depending on the matrix; typically 1g for oils and 30g for soils) is mixed with anhydrous sodium sulfate to form a free-flowing solid. Add hexane and extract three times using ultrasonic extraction. The extract is separated from the sample by centrifugation or through a filter paper. The extract is ready for cleanup and analysis.

3.0 INTERFERENCES

- 3.1 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate.
- 3.2 Degradation of PCBs, as well as more complex matrix (i.e. oil, tar, sulfur, etc.) can interfere with the "clarity" of the chromatograms.

4.0 APPARATUS AND MATERIALS

- 4.1 Apparatus for grinding dry waste samples
- 4.2 Ultrasonic device – Branson Sonifier, Model 450
- 4.3 Ultrasonic Disrupter - power wattage of 300 watts, with pulsing.
 - 4.3.1 3/4" horn
 - 4.3.2 Sonabox – (Ultrasonics #432B)
- 4.4 Apparatus for percent dry weight
 - 4.4.1 Drying oven (105°C - 120°C)
 - 4.4.2 Desiccator
 - 4.4.3 Crucibles – disposable aluminum
 - 4.4.4 Glass pipettes - 1ml, disposable
 - 4.4.5 Beakers – 250ml
 - 4.4.6 Filter paper - Whittman No. 41
- 4.5 Zymark Evaporation Station
- 4.6 Evaporation tubes
- 4.7 Water bath - Heated, capable of temperature control ($\pm 5^{\circ}\text{C}$).
- 4.8 Balance - Top-loading, capable of accurately weighing to the nearest 0.01 g.
- 4.9 Vials – 4 ml, with polytetrafluoroethylene (PTFE)-lined screw caps.
- 4.10 Glass scintillation vials - 20-mL, with PTFE-lined screw caps.
- 4.11 Tongue depressors, disposable
- 4.12 Drying column - 50ml Pyrex chromatographic column with Pyrex glass wool at bottom.
- 4.13 Syringe - 5-mL.

5.0 REAGENTS

Note: Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

- 5.1 Reagent water
- 5.2 Sodium sulfate (granular, anhydrous), Na_2SO_4 .
- 5.3 Extraction - All solvents must be pesticide quality or equivalent
 - 5.3.1 Hexane, C_6H_{14} , boiling point 68.7°C
 - 5.3.2 Nonchromix

6.0 SAMPLE CONTAINERS AND STORAGE

- 6.1 All samples for the analysis of Pesticides and PCBs should be stored in 4 oz. non-preserved glass containers only.
- 6.2 Approximately 2g to 30g (depending on the matrix) of sample is needed for extraction.
- 6.3 Refrigerate at 4°C .
- 6.4 Holding Time for solid samples is 14 days to extraction and 40 days after extraction

7.0 GLASSWARE CLEANING

- 7.1 Immediately after use rinse glassware with the last solvent used in it. Drain it into a bottle labeled "Wash Solvent"
- 7.2 Wash well with hot water and laboratory detergent by hand.
- 7.3 Rinse three times with hot tap water followed by three times with DI water.
- 7.4 Place in dishwasher.
- 7.5 Rinse with acetone.
- 7.6 Rinse with hexane.
- 7.7 All PCB glassware is placed in a furnace oven at 550°C for 12 hours prior to use. (This is done to avoid any cross contamination).
- 7.8 Separatory Funnels are washed with 40 ml hexane and evaporated to 1 ml final volume to analyze for cross contamination.

Note: All glassware must be immaculate. Glassware should be cleaned as soon as possible after the extraction. A quick reference guide is posted in the extraction laboratory. If the glassware is extremely dirty or has not been treated in more than a week, coat and soak it with concentrated H_2SO_4 preferably with Nonchromix added. Then rinse with tap water and follow the cleaning procedure above.

8.0 PROCEDURE^[1]

- 8.1 The extraction device has a minimum of 300 watts of power and is equipped with $\frac{3}{4}$ " size disrupter horns.
 - 8.1.1 The horn is maintained, by inspection of the horn tip for excessive wear that would be seen as "cavities" on the bottom of the instrument.
 - 8.1.2 Samples are prepared by thorough mixing with sodium sulfate so that it forms a free-flowing solid prior to the addition of the solvent.
 - 8.1.3 Three extractions are performed with hexane solvent.
 - 8.1.4 Extraction is performed in the specified pulse mode, and the horn tip is positioned just below the surface of the solvent yet above the sample.

^[1] Reference for this procedure is SW-846, Revision 3, December 1996 Method 3550B, Ultrasonic Extraction

- 8.1.5 Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. Observe such mixing at some point during the extraction process to insure that the placement of the horn is correct.
- 8.2 Sample handling
- 8.2.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.
- 8.2.2 Waste samples - Samples consisting of multiple phases are separated into two phases. Per client request one or the other phase is extracted. If both phases need to be extracted, two separate extractions are performed.
- 8.2.3 Dry waste samples amenable to grinding - Grind or drill the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Minimum of 10g of sample should pass through the sieve.
- 8.2.4 Gummy, fibrous, or oily materials not amenable to grinding are cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction.
- 8.3 Extraction method:
- 8.3.1 Weigh approximately 1-30 g of sample (depending on the matrix) into a 250-ml beaker. Typically, on a standard soil, 30 grams of sample is used. Record the weight to the nearest 0.1 g.
- 8.3.2 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using disposable tongue depressors. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.
- 8.3.3 Add 1.0 ml of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks.
- 8.3.4 For the sample in each batch selected for spiking (*i.e.* LCS, MS, MSD), add 1.0 ml of the matrix spiking solution.
- 8.3.5 Add 60 ml of Hexane to the beaker.
- 8.3.6 Place the bottom surface of the tip of the 3/4 inch disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer.
- 8.3.7 Extract ultrasonically for 3 minutes, with output control knob set at 6 and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time).
- 8.3.8 Decant through a conical gravity filter (Whatman No. 41 filter paper) and sodium sulfate to catch any excess water.
- 8.3.9 Repeat the extraction two or more times with an additional 60 ml portion of hexane. Pour off the solvent after each ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample onto the filter with extraction solvent.
- 8.4 Evaporation method
- 8.4.1 Place the concentrator tube in the TurboVap Evaporation Station, that has the water bath @ 42°C (+/- 2°C), 21 psi, until 1 ml final volume.
- 8.4.2 Transfer the sample extract to a 4 ml vial. Adjust up to 1 ml final volume.
- 8.4.3 Final 1 ml adjustment: if the transfer is greater than 1 ml, use the clean nitrogen gas to evaporate to the meniscus on the vial marked with a 1 ml mark and compare to the calibrated vial. If the transferred extract is less than 1 ml, add final extract solvent to the meniscus.
- 8.4.3.1 The vials are calibrated per Lot # of vials with a NIST traceable syringe. One vial is filled with exactly 1 ml for comparison.
- 8.4.4 Follow with clean -up procedures as appropriate for the analysis.

9.0 PCB CLEAN-UPS (SEE PCB ANALYSIS SOP FOR DETAILS)

- 9.1 Sulfuric Acid Clean-up^[2]
- 9.2 Sulfur Clean-up^[3]
- 9.3 Alumina Column Clean-up
- 9.4 Quality Control
- 9.5 Samples are extracted in batches of 20 samples or less. For every batch there should be an LCS, MS, and MSD/DUP depending on the clients request. All the reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample amount to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.
- 9.6 The surrogate standard must contain the following compounds TCX (tetrachloro-m-xylene) and DCBP (decachlorobiphenyl). The surrogate standard is prepared by the GC analyst at a concentration of 0.01mg/l.
- 9.7 The MS/MSD and LCS spikes will contain a mixture of Aroclor 1016/1260. MS/MSD spike should be prepared at a concentration at or below the medium level of the PCB curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.05mg/l.
- 9.8 New lot blanks are analyzed to insure the purity of the materials and reagents.

Note: The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced.

10.0 DOCUMENTATION

All pertinent information is entered into an extraction logbook (See Table 1). The extraction log sheet has to contain the following information on the header/table:

- Date
- ANALYSTS INITIALS
- Method
- Surrogate/MS/MSD/LCS standard unique traceability ID
- Hexane Lot #
- Sample I.D. #
- Matrix
- Sample weight
- Solvent ID & Volume (ml)
- Final extract volume
- Surrogate standard spike volume
- MS spike volume
- Additional clean-ups (i.e. alumina) are marked in the notes section as "C"

11.0 REFERENCES

11.1 Method 3550 SW

^[2] Reference for Sulfuric Acid clean-up is SW-846, Revision 3, December 1996 Method 3665A: Sulfuric Acid

^[3] Reference for Sulfur clean-up is SW-846, Revision 3, December 1996 Method 3660B: Sulfur Clean-up using copper.

12.0 APPROVAL & ISSUE:

Analyst

Date

Andy Ball, QC Officer

Date

Maya V. Murshak, QA Director

Date

SOP #043510: SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION
BY METHOD 3510C

Revision: 9
Date: 12/12/06

Location: Extraction Laboratory
GC/ECD Laboratory

These procedures are restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with these techniques and methods.

1.0 SCOPE AND APPLICATION

This SOP is a procedure for isolating organic compounds from aqueous samples. This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures, specifically PCBs and Pesticides.

2.0 SUMMARY OF METHOD

- 2.1 A measured volume of sample, usually 1 liter, at a pH 5-9, is extracted with methylene chloride using a separatory funnel.
- 2.2 The extract is concentrated, and, exchanged into hexane solvent which is also compatible with the cleanup procedures utilized for PCBs.
- 2.3 Clean glassware and matrix cleanup procedures are used to obtain the optimum analytical chromatograms.

3.0 INTERFERENCES

- 3.1 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may de-chlorinate.
- 3.2 Degradation of PCBs, as well as more complex matrices (i.e. oil, tar, sulfur, etc.) can interfere with the "clarity" of the chromatograms.

4.0 APPARATUS AND MATERIALS

- 4.1 Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.
- 4.2 Evaporation tubes, 250-ml volume, Zymark with end point of 0.5 ml.
- 4.3 Zymark Turbo Vap II Concentration Station with temperature control water bath.
- 4.4 Vials – 4 ml, glass with PTFE-lined screw caps or crimp tops.
- 4.5 pH indicator paper - pH range including the desired extraction pH.
- 4.6 Glass beakers, 250 ml.
- 4.7 Glass funnel and ring stand
- 4.8 Filter paper, coarse grade
- 4.9 Adhesive labels
- 4.10 Syringe - 5-mL NIST certified
- 4.11 Graduated cylinder - 1-liter

5.0 REAGENTS

Note: Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

- 5.1 Reagent water
- 5.2 Sodium sulfate (granular, anhydrous), Na_2SO_4 .
- 5.3 Sulfuric acid, concentrated, as well as solution (1:1 v/v), H_2SO_4 . Slowly add 50 mL of H_2SO_4 to 50 ml of DI water.
- 5.4 Extraction/exchange solvents - All solvents must be pesticide quality or equivalent

SOP #043510: SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION
BY METHOD 3510C

Revision: 9
Date: 12/12/06

- 5.4.1 Methylene chloride, CH_2Cl_2 , boiling point 49°C
- 5.4.2 Hexane, C_6H_{14} , boiling point 68.7°C
- 5.4.3 Nonchromix

6.0 SAMPLE CONTAINERS AND STORAGE

- 6.1 All samples for the analysis of Pesticides and PCBs should be stored in Amber glass containers only.
- 6.2 Approximately 1L volume of sample is needed for extraction.
- 6.3 Refrigerate at 4°C .
- 6.4 The holding time for samples is 7 days until extraction and 40 days thereafter.

Note: If samples contain significantly less volume than 1L, QA & client need to be notified. Higher detection limits will be applied to low volume extracts.

7.0 GLASSWARE CLEANING

- 7.1 Immediately after use rinse glassware with the last solvent used in it. Drain it into a bottle labeled "Wash Solvent"
- 7.2 Wash well with hot water and laboratory detergent by hand.
- 7.3 Rinse three times with hot tap water followed by three times with DI water.
- 7.4 Place in dishwasher.
- 7.5 Rinse with acetone.
- 7.6 Rinse with hexane.
- 7.7 All PCB glassware is placed in a furnace oven at 550°C for 12 hours prior to use. (This is done to avoid any cross contamination).
- 7.8 Separatory Funnels are washed with 40-ml hexane and evaporated to 1-ml final volume to analyze for cross contamination.

Note: All glassware must be immaculate. Glassware should be cleaned as soon as possible after the extraction. A quick reference guide is posted in the extraction laboratory. If the glassware is extremely dirty or has not been treated in more than a week, coat and soak it with concentrated H_2SO_4 preferably with Nonchromix added. Then rinse with tap water and follow the cleaning procedure above.

8.0 PROCEDURE^[1]

- 8.1 Mark the level of sample on the outside of the bottle. Sample volume needed for extraction should be close to 1L. Pour the sample into the 2-liter separatory funnel.
- 8.2 Pipette 1.0 ml of the surrogate spiking solution into the funnel and swirl the sample.
 - 8.2.1 For matrix spike samples and LCS, add 1ml surrogate and 1 ml matrix spike standard.
 - 8.2.2 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to a pH between 6 – 9.
- 8.3 Add 60 ml of methylene chloride into the sample bottle to rinse it and transfer this rinse solvent to the separatory funnel.
- 8.4 Shake the separatory funnel vigorously for 1 minute on a vertical placement with full ventilation at motor speed 68. Seal the separatory funnel and shake vigorously for 2 minutes on a horizontal placement at motor speed 70 in accordance with Table 1 shake program. Initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors. Allow the organic layer to separate from the water phase for 1 to 10 minutes, depending on the matrix of the sample.

^[1] Reference for this procedure is SW-846, Revision 3, December 1996 Method 3510C, Liquid Liquid Separatory Funnel Extraction

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Note: If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

- 8.5 Drain the extract through a filter filled with approximately 10g of Na₂SO₄ into a 250-ml glass Zymark evaporation tube.
 - 8.6 Add 60ml methylene chloride to the separatory funnel. Seal and shake the separatory funnel vigorously for 1 minute on a horizontal placement at motor speed 74. Vent the funnel and continue for 2 minutes in accordance with Table 1 shake program. Initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors. Allow the organic layer to separate from the water phase for 1 to 10 minutes, depending on the matrix of the sample.
 - 8.7 Repeat step 8.6 once more with 60ml methylene chloride each in accordance with Table 1 shake program.
 - 8.8 After all of the extract solvent has been collected, place the evaporation tube into the Turbo Vap II evaporation station, with the bath water at 42°C +/- 2°C and 21 psi. Allow the sample to evaporate down to 1ml methylene chloride or until the evaporation station signals completion. Use nitrogen to blow down the sample to make sure that it does not spill out.
 - 8.9 Add 30 ml hexane and evaporate down to 1ml final volume under the same conditions as above.
 - 8.10 Transfer the final volume into a pre-calibrated 4-ml glass vial, rinse the evaporation tube with clean Hexane and bring to 1-ml. If the final volume is over 1ml, use nitrogen gas or a special airline to evaporate to the 1-ml mark.
 - 8.11 Final 1 ml adjustment: if the transfer is greater than 1 ml, use the clean nitrogen gas to evaporate to the meniscus on the vial marked with a 1 ml mark and compare to the calibrated vial. If the transferred extract is less than 1 ml, add final extract solvent to the meniscus.
 - 8.11.1 The vials are calibrated per Lot # of vials with a NIST traceable syringe. One vial is filled with exactly 1 ml for comparison.
 - 8.12 Find the original volume of the sample by pouring tap water into the sample container to the mark. Pour the water into a 1000 ml graduated cylinder, and record the volume in the extraction logbook and label.
- 9.0 PCB CLEAN-UPS (SEE PCB ANALYSIS SOP FOR DETAILS)
- 9.1 Sulfuric Acid Clean-up^[2]
 - 9.2 Sulfur Clean-up^[3]
 - 9.3 Alumina Column Clean-up
- 10.0 QUALITY CONTROL
- 10.1 Samples are extracted in batches of 20 samples or less. For every batch there should be an LCS, MS, and MSD/DUP depending on the client's request. All the reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples. In case of the client not providing the necessary sample volume to perform the required QC samples, equivalent laboratory matrix samples can be analyzed.
 - 10.2 The surrogate standard must contain the following compounds TCX (tetrachloro-m-xylene) and DCBP (decachlorobiphenyl). The surrogate standard is prepared by the GC analyst at a concentration of 0.01mg/l.

^[2] Reference for Sulfuric Acid clean-up is SW-846, Revision 3, December 1996 Method 3665A: Sulfuric Acid

^[3] Reference for Sulfur clean-up is SW-846, Revision 3, December 1996 Method 3660B: Sulfur Clean-up using copper.

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10.3 The MS/MSD and LCS spikes will contain a mixture of Aroclor 1016/1260. MS/MSD spike should be prepared at a concentration at or below the medium level of the PCB curve. The MS/MSD and LCS standard is prepared by the GC analyst at a concentration of 0.05mg/l.

10.4 New lot blanks are analyzed to insure the purity of the materials and reagents.

Note: The working standards are prepared every six to 12 months or when evidence of bias or trends are observed to show that the standards need to be replaced.

11.0 DOCUMENTATION

All pertinent information is entered into an extraction logbook (See Table 1). The extraction log sheet has to contain the following information on the header/table:

- Date
- ANALYSTS INITIALS
- Method
- Surrogate/MS/MSD/LCS standard unique traceability ID
- Hexane & Methylene Chloride Lot #
- Sample I.D. #
- Matrix
- Sample volume
- Solvent ID & Volume (ml)
- Final extract volume
- Surrogate standard spike volume
- MS spike volume
- Additional clean-ups (i.e. alumina) are marked in the notes section as "C"

12.0 REFERENCES

12.1 Method 3510 SW

13.0 APPROVAL & ISSUE:

13.1 The following personnel have read, accepted and approved this standard operating practice.

Analyst

Date

Andy Ball, QC Officer

Date

Maya V. Murshak, Technical Director

Date

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13.0 TABLES

Table 1. Extraction Funnel Shake Program

Stage	Solvent Volume	pH	Funnel Position	Shaker Time	Shaker Intensity
1	60 ml	5-9	horizontal/closed	3 min	70
2	60 ml	5-9	horizontal/closed	3 min	70
3	60 ml	5-9	horizontal/closed	3 min	70

Location: Metals Laboratory
QA Officer's Office
SOP Files

1.0 SCOPE AND APPLICATION

- 1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable for the determination of sub- $\mu\text{g/L}$ concentrations of a large number of elements in water samples and in waste extracts or digestions. When dissolved constituents are required, samples are filtered through 0.45 μm membrane filters and acid-preserved prior to analysis. No digestion is needed prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is performed for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are needed. Acid digestion is also needed prior to analysis to dissolve elements in drinking water samples with turbidity <1 NTU. This SOP follows the guidelines of the EPA Methods 200.8, 6020, and 6020A.
- 1.2 The metals that are determined by using this SOP are listed in Table 1 with examples of reporting limits and which methods can be used for each element.
- 1.3 If this SOP is followed to determine any analyte not listed in Table 1, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method as well as method detection limit (MDL) and multi-point calibration. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality.
- 1.4 Use of this SOP is restricted to analysts who are knowledgeable in the recognition and in the correction of spectral, chemical and physical interferences in ICP-MS.

2.0 SUMMARY OF METHOD

- 2.1 Prior to analysis, samples which require total ("acid-leachable") values are digested using appropriate sample digestion procedures (SOP # 083015 and # 083050B). See Digestion prep log in Appendix 3.
- 2.2 This SOP describes the measurement of ions produced by radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios, and quantified with a channel electron multiplier. Potential interference from isobaric elements and polyatomic ions are corrected for by the use of elemental interference equations based on natural isotope abundance. Interference corrections include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix. Instrument drift and matrix induced signal suppressions and enhancements are compensated for by the use of internal standardization.

3.0 INTERFERENCES

There are three fundamentally different sources of interference in ICP-MS: spectroscopic interferences, physical interferences, and memory interferences.

- 3.1 **Spectroscopic Interferences** are interferences caused by the presence of compounds or elements entering the mass spectrometer which have the same nominal mass-to-charge (m/z ratio of the analyte elements). They can be isobaric elemental and isobaric molecular interferences (polyatomic, refractory oxide, and doubly charged ions).
 - 3.1.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) as the analyte element. These are managed by the selection of an alternate isotope for analysis or by the use of elemental interference equations. These equations use the naturally occurring isotope ratios of most elements to estimate and allow for the subtraction of isobaric interferences. An example of an elemental isobaric interference is ^{40}Ar on ^{40}Ca . In this case, the use of ^{43}Ca or ^{44}Ca is recommended. The appropriate elemental interference equations are incorporated in the methods (or parameter) used for calibration and data acquisition.
 - 3.1.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that

affect ICP-MS determinations have been identified. Examples include ArCl^+ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundance, the most precise coefficients for an instrument is determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting statistics.

3.1.2.1 Example for As is as follows: Because the ^{35}Cl natural abundance of 75.77% is 3.13 times the ^{37}Cl abundance of 24.23%, the chloride correction for arsenic is calculated (approximately) as follows (where the $^{38}\text{Ar}^{37}\text{Cl}^+$ contribution at m/z 75 is a negligible 0.06% of the $^{40}\text{Ar}^{35}\text{Cl}^+$ signal): Corrected arsenic signal (using natural isotopes abundance for coefficient approximations) = (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), (where the final term adjusts for any selenium contribution at 77 m/z).

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}\text{Se}^+$ (e.g., $^{81}\text{BrH}^+$ from bromine wastes⁶).

3.1.2.2 Example for Cd is as follows: corrected cadmium signal (using natural isotopes abundance for coefficient approximations) = (m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal), (where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

NOTE: Cadmium values are biased low by this type of equation when $^{92}\text{ZrO}^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}\text{ZrOH}^+$) and indirect ($^{90}\text{ZrO}^+$) additive interferences when Zr is present.

NOTE: Since there is a certain degree of uncertainty as to which equation is better to use, and in what cases, it is up to the analyst to determine how the interference is corrected, upon the evaluation of data. It is suggested that the elemental isobaric interference equations be included in all methods (parameters) from the beginning, but potential polyatomic species (masses) that could interfere be only monitored (except for $^{40}\text{Ar}^{35}\text{Cl}^+$ on As). When species monitored indicate that an isobaric molecular interference is present, the equations can be adjusted to correct for such interference, and data be reprocessed to produce an interference free summary report. Generally, an interference is easy to spot when multiple isotopes of an element show different results. Since the interference is additive, the use of the isotope with the lowest result is suggested for data reporting, providing that all other QC criteria are met (See Table 6 for summary of QC requirements).

3.1.3 Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. Wing overlap interference can occur when a small ion peak is being measured adjacent to a large one. The potential for these interferences must be recognized, and the spectrometer resolution adjusted to minimize them. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require matrix separation, or analysis using another verified and documented isotope.

3.2 **Physical Interferences** are associated with the physical processes, which govern the transport of sample into the plasma, sample conversion process within the plasma and the transmission of ions through the plasma-mass spectrometer interface. These interferences can result in differences between instrument responses for the samples and calibration standards. Physical interferences can occur in the transfer of solution to the nebulizer (e.g. viscosity effects), at the point of aerosol formation and transport to the plasma (e.g. surface tension effects), during the atomization and ionization process within the plasma itself, or during the transfer of ions through the interface and mass spectrometer (space charge effects). To minimize some of these effects, acid composition and concentration must be matched for all standards, blanks, and samples. Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. Internal standardization is effectively used

to compensate for many physical interference effects. Internal standards must ideally display similar analytical behavior to the elements being determined. Generally, an internal standard must be no more than 50 amu removed from the analyte. Recommended internal standards include ^6Li , ^{45}Sc , ^{89}Y , ^{103}Rh , ^{115}In , ^{159}Tb , ^{169}Ho , ^{185}Re , and ^{209}Bi .

- 3.3 **Memory Interferences** result when elements in a previous sample contribute to signals measured in a subsequent sample. Memory effects can result from the deposition of sample on various components of the sample introduction system, including sample and peristaltic pump tubing, spray chamber, torch, and interface cones. The site(s) where deposition can occur is dependent on the sample and needs to be minimized through the use of a rinse blank between samples. Routine maintenance (cleaning and/or replacement) of sample introduction components is necessary for long-term minimization of memory effects. The possibility of memory interferences within an analytical run must be recognized and suitable rinse times must be used to reduce them. Memory effects are evaluated by using a minimum of three replicate integrations for data acquisition. High relative standard deviation (%RSD) of the three replicates caused by a consecutive drop in signal intensity is indicative of carryover from the previous sample. If a memory interference is suspected, the sample must be reanalyzed after analysis of a blank indicates that the carryover has been eliminated.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled plasma-mass spectrometers:

4.1.1 **Perkin Elmer (PE) Elan 9000 ICP-MS:**

- Windows XP Operating System
- Elan 3.0 Software
- Cetac Asx510 Autosampler

4.1.2 **Hewlett-Packard (HP) 4500 ICP-MS:**

- Windows 95 Operating system.
- Chem Station Software.
- Cetac ASX150 Autosampler.

4.1.3 **Agilent 7500Ce ICP MS**

- Windows XP Operating system
- Chem Station Software
- Agilent ASX 500 Series autosampler

4.2 Argon gas supply: liquid argon cylinders

4.3 Analytical balance, 510 g capacity, minimum accuracy ± 0.001 g

4.4 Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments

4.5 Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 μl to 5,000 μl

Note: dispensers are calibrated quarterly according to SOP #010010

4.6 Disposable Pasteur pipettes

4.7 Polypropylene vessels, 50 mL

4.8 Plastic cups to support minimum of 200 ml

4.9 Plastic bottles

5.0 REAGENTS & STANDARDS

5.1 Nitric Acid (HNO_3), concentrated, Trace Metal Grade. Acids used in the preparation of standards and for sample processing must be of high purity. Trace metal grade (also known as re-distilled) acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at 2% (v/v) or less in the solution to be analyzed is required for ICP-MS, in order to minimize damage to the interface.

5.2 Hydrochloric Acid (HCl), concentrated, Trace Metal Grade. Several polyatomic ion interferences result when HCl is used. However, its use is recommended to maintain stability in solutions containing high concentrations of antimony and silver. When used, corrections for the chloride polyatomic ion interference must be applied to all data.

5.3 Reagent water (Deionized water): All references to reagent water in the method refer to ASTM Type I water (ASTM D1193), unless otherwise specified.

5.4 Internal Standard stock solutions:

5.4.1 Lithium 6, 1000 $\mu\text{g/ml}$ stock solution.

5.4.2 Scandium, 1000 $\mu\text{g/ml}$ stock solution.

- 5.4.3 Yttrium, 1000 µg/ml stock solution.
- 5.4.4 Rhodium, 1000 µg/ml stock solution.
- 5.4.5 Rhenium, 1000 µg/ml stock solution.
- 5.4.6 Internal Standard Working Solution (IS-WS): From the above stock solution, 2.5 ml of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO₃ and brought to a final volume of 1000 ml (by weight), which corresponds to 2.5 µg/ml. This represents the internal standard working solution from which 1 ml (for a 50 ml final volume) must be added to all calibration standards and blanks. This provides a 0.05 ppm of internal standard concentration in all calibration standards, similar to analytical samples.

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor. See Appendix 1 for blank page of standard preparation log book page.

- 5.5 Multi-element standard stock solution from three of four different vendors:
 - 5.5.1 Inorganic Venture (IV), 100 mg/L each of Ag, Al, B, Ba, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, Tl, V, and Zn. This solution is used for the preparation of standards.
 - 5.5.2 High Purity Standards (HM), 100 µg/ml each of Ca, Mg, K, and Na. This solution is used for the preparation of the calibration standards and for the minerals standard.
 - 5.5.3 SPEX Industries (S), 100 µg/ml each of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Se, Si, Ag, Na, Sr, Sn, Ti, Tl, V, and Zn. This solution is used for the preparation of the initial calibration verification (ICV) standards.
 - 5.5.2 Environmental Resource Associates (ERA), concentration varies by lot number and element but contains all of the following Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Ag, Zn, V, Th, and S.

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor. See Appendix 1 for Standard Prep Log and Appendix 2 for ICV prep log.

- 5.6 Multi-element calibration standard solutions are prepared by diluting the stock standard solutions to levels in the linear range for the instrument in a solvent consisting of 2% (v/v) HNO₃ in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. The calibration standards are kept in plastic bottles and prepared every two weeks or more frequent if needed. They must be verified using a quality control standard (ICV). Table 2 (metals) and Table 3 (minerals) are used as guidance, when preparing standards.
- 5.7 Blanks: Three types of blanks are required for the analysis. The calibration blank (std-0.00) is used in establishing the calibration curve. The Laboratory Reagent Blank (LRB) also known as method blank is used to monitor possible contamination resulting from the sample preparation procedure. The rinse blank (also called optional rinse or autosampler wash) is used to flush the system between all samples and standards.
 - 5.7.1 The calibration blank (std-0.00), the initial calibration blank (ICB), and the continuing calibration blank (CCB) consists of the same concentration(s) of the same acid(s) used to prepare the calibration standards, along with the appropriate concentration of internal standard. The preparation of these blanks can be found in the standards prep-log. The calibration blank is used in the calibration process, the ICB is used to check the instrument before analyzing samples, and the CCB is used to verify the instrument in the middle and end of analytical runs.
 - 5.7.2 The Laboratory Reagent Blank (LRB) also known as method blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.
 - 5.7.3 The rinse blank consists of 2% HNO₃ (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples. Rinse blank is prepared by adding 20 ml of concentrated HNO₃ to 1000 ml of DI water in a large plastic container.
- 5.8 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interference such as ³⁵Cl¹⁶O⁺ on ⁵¹V⁺ and ⁴⁰Ar³⁵Cl⁺ on ⁷⁵As⁺. Iron is used to demonstrate adequate

resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

- 5.8.1 Interference check stock solution A, containing 1000 µg/ml each of Al, Ca, Fe, Mg, Na, P, K, and S, 2000 µg/ml of C, 10000 µg/ml of Cl, and 20.0 µg/ml each of Mo and Ti. The ICS-A solution is prepared by weighing 10.0 g of the stock solution in a plastic cup, addition of 2 ml IS-WS, 2 ml HNO₃, and dilution to 100 g on the scale with reagent water.
 - 5.8.2 Interference check stock solution AB, containing 2.0 µg/ml each of As, Cd, Cr, Co, Cu, Mn, Ni, Ag, and Zn. The ICS-AB solution is prepared by weighing 1.00 g of the stock solution in a plastic cup, addition of 2 ml IS-WS, 2 ml HNO₃, and dilution to 100 g on the scale with reagent water.
 - 5.8.3 The final concentration of the elements in ICS-A and ICS-AB is listed in Table 4. These solutions are prepared fresh every two weeks or as needed.
 - 5.9 The initial calibration verification solution (ICV) is used to verify the calibration before samples are analyzed. The ICV must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard (known as a second source) is defined as a standard from a source different from those used in the standards for instrument calibration.
 - 5.10 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Section 7.5). This solution is also used to verify that the instrument has reached thermal stability (See Section 7.4).
 - 5.10.1 Tuning solution for HP 4500 ICP-MS: 10 µg/ml each of Li, Y, Ce, and Tl is used to tune the instrument according to the manufacturer instructions.
 - 5.10.2 Tuning solution for PE Elan 9000 and Agilent 7500Ce ICP-MS: 10µg/ml each of Li 7, Be 9, Mg 25, Co 59, In 115, Tl 205, and Pb 208.
 - 5.11 Working standards and solutions are prepared every two weeks according to recipes in the standards prep log. The logbook is available in the metals lab. Concentrations of the LCS can be found on the laboratory bench sheet.
- 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING
- 6.1 All samples are collected in appropriate containers. For water samples, the samples are collected in HNO₃ pre-preserved plastic container (approximately 125 ml volume), and are acidified to pH of <2.
 - 6.2 Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples must be refrigerated at 4 ±2 C° upon receipt.
 - 6.3 Holding times for metals are 6 months from the date of sampling to analysis. For TCLP samples the holding time is 6 months from sampling to TCLP extraction then 6 months from TCLP extraction to analysis.
- 7.0 PROCEDURE
- 7.1 Solubilization and digestion procedures are presented in the Sample Preparation SOPs (# 083015 and/or #083050B). A sample digestion log sheet is found in Appendix 3.
 - 7.2 Initiate appropriate operating configuration of the instrument's computer according to the instrument manufacturer's instructions.
 - 7.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.
 - 7.4 Operating conditions: The analyst must follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. The thermal stability must be verified by analyzing a tuning solution described in Section 5.10.1, and 5.10.2.
 - 7.5 For all analysis tune instrument according to following parameters.
 - 7.5.1 The tuning must include beryllium, magnesium, cobalt, indium, and lead. Conduct mass calibration and resolution checks in the mass regions of interest.

- 7.5.2 The mass calibration and resolution parameters are required criteria that must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value.
- 7.5.3 The resolution must be verified to be within 0.6-0.9 amu full width at 5 percent peak height (not applicable for HP4500 ICP-MS due to manufacturer presets).

Note: A peak height of 5 percent is used instead of 10 percent because 5 percent is the tighter restriction and this SOP is written to meet the requirements of methods 200.8, 6020, and 6020A.

- 7.5.4 Perform tune after machine is warmed up and every 12 hours following.

NOTE: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

- 7.6 The instrument is calibrated daily and re-calibrated as needed. Calibrate the instrument for the analytes of interest (recommended isotopes for the elements in Table 1 are provided in Table 5a and Table 5b), using the calibration blank and at least three non-zero calibration standards according to the instrument manufacturer's procedure. A multi-point calibration curve is analyzed and evaluated. For the calibration curve to be acceptable, a correlation coefficient of greater than or equal to 0.998 must be achieved. If the required correlation coefficient is not achieved then the extreme upper and lower calibration points may be removed from the multi-point curve as long as three non-zero points remain such that the linear range is narrowed and the non-linear upper and/or lower portions are removed. If narrowing the linear range does not improve the correlation coefficient to 0.998, then replace the calibration standards and re-calibrate the instrument. The reporting limit (RL) must be greater than or equal to the lowest calibration point or the concentration of low level initial calibration verification (LLICV) which ever is lower.

The principle of calculation for the linear curve fit and the coefficient of determination (COD) is found in SW 846 method 8000C Sections 11.5.2.1 through 11.5.2.3. ICP-MS manufacture software is preprogrammed for this calculation.

The multi point calibration is verified with a mid level ICV standard with control limits of 90%-110% and a low-level ICV with limits of 70%-130%. Table 2 and Table 3 (Section 5.6) provide information to what calibration standards are used. (More information on limits and corrective actions can be found in Section 8 and Table 6). Flush the system with the rinse blank (Section 5.7.3) between each standard solution. The instrument must be set to use the mean of at least three integrations for both calculation of calibration points and the calculation of sample concentrations.

- 7.7 All masses that affect data quality must be monitored to determine potential effects from matrix components on the analyte peaks. Preferred isotopes are referenced in Tables 5a and 5b.
- 7.8 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the initial calibration verification solution (ICV, Section 5.9) using a second source standard. When measurements exceed $\pm 10\%$ of the true value, the analyses must be terminated, the problem corrected, the instrument re-calibrated, and the new calibration verified. During the course of an analytical run, the instrument may require re-calibration to correct for instrument drift. A re-calibration must then be followed immediately by a new analysis of a ICV, LLICV, and initial calibration blank (ICB) before any further samples are analyzed. Corrective actions for specific situations are found in Section 8 and summarized in Table 6.
- 7.9 A low-level initial calibration verification (LLICV) must be analyzed after every calibration to verify the linearity near the lower end of the calibration curve. The LLICV is made from the same source as the calibration standards at a concentration comparable to the reporting limits of elements being reported. When the LLICV measurements exceed $\pm 30\%$ of the true value, the analyses must be terminated, the problem corrected, the instrument re-calibrated, and the new calibration verified. (limits and corrective action information can be found in Section 8 and is summarized in Table 6).

- 7.10 Flush the system with the rinse blank solution (Section 5.7.3) until the signal levels return to the method's levels of quantitation (usually about 30 seconds) before the analysis of each sample. Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (CCV), and the continuing calibration blank (CCB) at a frequency of at least once every 10 analytical samples (limits and corrective action information can be found in Section 8 and is summarized in Table 6).
- 7.11 Dilute and reanalyze samples that are more concentrated than the linear range (LR) (Section 8.2.2) for an analyte or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (Sections. 7.6 through 7.8).
- 7.12 Interference Check Solutions (ICS) are run to verify the magnitude of elemental and molecular-ion isobaric interferences. This is performed every 12 hours. This is done by analyzing interference check solutions A and AB. (Concentration of elements in solution found in Table 4, other reagent information is in Section 5.8)
Corrective Action: The ICS needs to be within 70-135%. If the ICS fails, re-evaluate the equations used for the corrections, make the necessary adjustments, recalibrate the instrument and re-analyze the samples associated with the failed ICS. See Table 6 for ICS summary and Section 8.10.2.2 for more information.

Note: Precipitation from solution AB can occur with some elements, specifically silver. Rinse the instrument 5 –10 minutes before analyzing any other samples to help improve performance.

- 7.13 Calculations: The quantitative values are reported in appropriate units, such as milligrams per liter (mg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples.
- 7.13.1 The appropriate dilution factor (DF) on water samples resulted from sample preparation (see SOPs #083015 and #083050B) is entered in the data system for each sample at the time of programming the sequence to be analyzed. If additional dilutions are performed, the appropriate corrections must be applied to the dilution factor, using the following equation

$$C \times DF = SC$$

Where, C = digest concentration

DF = Dilution Factor

SC = Sample Concentration

The ICP/MS software carries out this calculation for the analyst.

- 7.13.2 Generally, for solid samples, DF includes the correction necessary for the determination of a dry weight result. If this is not the case or if a dry weight result is requested at a later time, calculate results for solids on a dry-weight basis as follows:

- (1) A separate determination of percent solids must be performed.
- (2) A new DF is calculated, based on the original wet weight of the sample (from the preparation log) and the percent total solids. The sequence is updated with the new DF, data reprocessed, and a new quantitation report is generated by the data system.
- (3) Manual calculation of the dry weight concentration (DWC) by the formula:

$$DWC \text{ (mg / kg)} = \frac{CxV}{W \times S}$$

Where, C = Digest Concentration (mg/L).

V = Final volume in liters after sample preparation.

W = Weight in kg of wet sample.

S = (% Total Solids)/100.

- 7.13.3 Calculations performed by the data system include appropriate interference corrections, internal standard normalization, and the summation of signals (for example 206, 207 and 208 m/z for lead) to compensate for any differences in the abundances of these isotopes between samples and standards.

Note: The instrument must be set to use the mean of at least three integrations for both calculation of calibration points and the calculation of sample concentrations.

8.0 QUALITY CONTROL

- 8.1 All quality control data must be maintained and be available for easy reference or inspection.
- 8.2 Demonstration of Performance
 - 8.2.1 The demonstration of performance is used to demonstrate instrument performance and has two parts. The first is initial demonstration of performance this is done by performing method detection limit (MDL) studies, linear range studies, and precision and accuracy studies prior to the analysis of samples. The second is continual demonstration of performance is done by annual MDLs and linear range studies. MDL studies are performed by following SOP #060004 (Determination of Method Detection Limit). Analyst performance is demonstrated by analysis of proficiency test and blind samples multiple times per year.
 - 8.2.2 Linear calibration ranges: Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range must be established by determining the signal responses from a minimum of five different concentration standards. Care must be taken to avoid potential damage to the detector during this process. The linear calibration range, which is used for the analysis of samples, must be judged by the analyst from the resulting data. The upper LR is defined as the maximum concentration for which the measured concentration is within $\pm 10\%$ of the true value. Determined sample analyte concentrations that are greater than the upper LR limit must be diluted and reanalyzed. The LR must be verified whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined. See Section 7.6 for curve specific criteria.
- 8.3 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If an interference source is present, and can not be corrected, the sample elements impacted must be flagged. The ICS is used to verify the correction equations used by the instrument. Requirements are found in Section 8.10.2.2 and Table 4 and preparation information is in Section 5.8.
- 8.4 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard falls outside the control limits as compared with the first calibration standard (Calibration Blank or std-0.00), the following procedure is followed. Check for instrument drift, instrument drift is characterized by internal standards outside control limits for QC samples (Section 8.10.1.4), recalibrate instrument and reanalyze samples. If matrix interference is suspected, the sample must be diluted at least fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal standard intensities fall within the prescribed window. (Summary of control limits and corrective actions can be found in Table 6)
 - 8.4.1 The intensity levels of the internal standards for the ICV/ICB/LLICV, CCV/CCB, LCS/LRB must also be within the specified acceptance limits (refer to Section 8.10.1.4 for limits and Sections 7.6-7.12 for procedure information). If they are not within limits, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.
- 8.5 Check the instrument calibration by analyzing appropriate quality control solutions as follows (Summarized in Table 6):
 - 8.5.1 Initial Calibration must include a blank and minimum of three non-zero points. A correlation coefficient of 0.998 must be achieved. Section 7.6 for calibration procedure.
 - 8.5.2 Immediately after instrument calibration check instrument calibration by analyzing the ICV described in Section 5.9. ICV limits are 90%-110% and the ICB. The ICB has to be less than the lower limit of quantitation for every target element. The lower limit of the calibration must be checked by analyzing the low-level initial calibration verification (LLICV) with acceptance limits of 70%-130%. Summary of limits and corrective actions are found in Table 6, the procedure for this is found in Sections 7.6 through 7.9.
 - 8.5.3 When running samples verify calibration at a frequency of every 10 analytical samples with the CCV standard with limits of 90-110% and the continuing calibration blank (CCB) with acceptance criteria of less than the lower limit of quantitation for every target element. These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed. See Table 6 for summary of

acceptance criteria and corrective actions, the procedure for this information for this is found in Section 7.10.

- 8.5.4 Corrective action for out of compliance ICV, LLICV, and CCV, is to terminate the analysis, correct the problem, and recalibrate the instrument. Control limits and corrective actions are found in Section 8.10 and summarized in Table 6.
- 8.6 Laboratory Reagent blank (LRB) also known as Method blank. Method blank (LRB) must be carried throughout the entire sample preparation and analytical process. The LRB is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method and then carried through the appropriate analytical process. The LRB has to be below the RL divided by the dilution factor for each target analyte. If the LRB does not contain target analytes at a level that interferes with the project specific requirements, then the LRB is acceptable. Control limits and corrective actions are summarized in Table 6.
- 8.7 A Laboratory Control Sample (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods, and QA/QC procedures employed for the test samples. One LCS must be prepared and analyzed for each sample batch at a frequency of one LCS for a least every 20 samples or every 10 samples for drinking waters. The recovery limits for the LCS are 85-115% of the true value (stated in the preparation log). If the LCS is outside of the control limits the entire sample batch must be re-digested and re-analyzed. Control limits and corrective actions are summarized in Table 6. (In method 200.8, the LCS is referred to as the Laboratory Fortified Blank, LFB)
- 8.8 Analyze one matrix spike (MS) sample for every 10 analytical water samples or every 20 analytical soil samples. For majority of the elements, the aqueous samples are spiked at levels similar to the LCS (0.05 ppm in the analysis solution). For solid samples, a concentration of 0.10 mg/kg is added pre-digestion. The acceptable limits for performance are summarized in Section 8.10 and Table 6.
- 8.8.1 Calculate the percent recovery of each analyte, corrected for background concentrations measured in the unfortified (original) sample. Percent recovery must be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{S} \times 100$$

where: R = percent recovery.

C_s = spiked sample concentration.

C = sample background concentration.

S = concentration equivalent of analyte added to fortify the sample.

- 8.9 Analyze one matrix duplicate (Dp) sample for every 10 water samples or every 20 soil samples. In some cases, a matrix spike duplicate (MSD) is used instead of the matrix duplicate, especially if the analytes in the sample are of low concentration. A control limit of 20% RPD must not be exceeded for analyte values greater than 100 times the MDL. If this limit is exceeded and laboratory performance for that analyte is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the problem encountered is judged to be matrix related. The data user must be informed that the result for that analyte is suspect due to the heterogeneous nature of the sample. If the performance of the laboratory is not in control (ICV/ICB, CCV/CCB, and LCS/LRB outside the limits), the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition for that analyte must be reanalyzed. Control limits and corrective actions are summarized in Table 6.
- 8.9.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} \times 100$$

where: RPD = relative percent difference.

D₁ = first sample value.

D₂ = second sample value (duplicate).

- 8.10 The Quality Control requirements and limits vary slightly, based upon the method referenced in the analytical report (i.e. 6020A vs. 200.8). For both methods, the calibration is verified by the analysis of ICV/ICB and CCV/CCB. Recalibration is required when either one falls outside the limits. The performance of the method is evaluated by the analysis of the LCS/LRB pair for every batch of 20 samples, and MS/MSD/Dp for every 10 water samples and 20 soil samples. The acceptable limits for performance are summarized in Table 6 and the procedures can be found in Sections 7.6 –through 7.12.
- 8.10.1 Requirements for all methods:
- 8.10.1.1 When the recovery for ICV/CCV falls outside $\pm 10\%$ terminate the analysis and recalibrate the instrument. The samples from the last CCV that was within limits are to be re-analyzed, after recalibration of the instrument.
 - 8.10.1.2 The MS is represented by a spiked sample, before digestion, and a Post-Digestion Spike, if the recovery of the regular spike fails to meet QC criteria. An analyte spike added to a portion of a prepared sample, or its dilution, must be recovered to within 75 to 125 percent of the known value. The spike addition must be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample is spiked and re-analyzed according to Figure 1. The same recovery limits apply to the spiked dilution.
 - 8.10.1.3 The MSD is represented by a spiked duplicate sample, before digestion, and a Post-Digestion Spike, if the recovery of the regular duplicate spike fails to meet QC criteria. The evaluation of the MSD is similar to the evaluation of the duplicate analysis described in Section 8.9.
 - 8.10.1.4 When the intensity of any internal standard in the sample to falls outside 70-125% of the intensity of that internal standard in the initial calibration standard (Calibration Blank or std-0.00), follow the procedure described in Section 8.4. The intensity levels of the internal standards for the ICV/LLICV/ICB and CCV/CCB must agree within ± 20 percent of the intensity level of the initial calibration standard (Calibration Blank or std-0.00). If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.
- 8.10.2 Method 6020/6020A specific requirements:
- 8.10.2.1 Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 x MDL), an analysis of a fivefold (1+4) dilution must agree within $\pm 10\%$ of the original determination. If not, an interference effect must be suspected, and the results flagged. One dilution test must be included with every batch of twenty samples.
 - 8.10.2.2 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. This is done by analyzing the interference check solutions ICS-A and ICS-AB. The recovery of the elements of interest in ICS-AB (listed in Table 4 at a concentration of 0.02 ppm) must be between 70-135% (see Section 7.12 for procedure information and Table 6 for a summary).
 - 8.10.2.3 The LLICV is used to verify the linearity of the low end of the calibration curve. The LLICV must be analyzed after every new calibration with the measurements not exceeding $\pm 30\%$ of the true value. If the LLICV is out side of these limits the run must be stopped and the instrument recalibrated and the new calibration verified (see Section 7.9 for procedure information and Table 6 for a summary).

9.0 WASTE DISPOSAL

- 9.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.
- 9.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

10.0 Safety

- 10.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.

- 10.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit.
- 10.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.
- 10.4 Specific attention be paid (but not limited) to
- 10.4.1 Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.
 - 10.4.2 Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.
 - 10.4.3 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.
 - 10.4.4 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

11.0 METHOD PERFORMANCE

- 11.1 The precision and accuracy of the method depends upon the overall performance of the sample preparation and analysis.
- 11.2 Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.
- 11.3 In an EPA multi-laboratory study, laboratories applied the ICP-MS technique to both aqueous and solid samples. The results are listed at the end of methods 200.8, 6020 and 6020A.

12.0 Definitions

- 12.1 Laboratory Control Sample (LCS) also known as the Laboratory Fortified Blank.
- 12.1.1 A laboratory control sample consists of either a control matrix spiked with analytes representative of the target analytes or a certified reference material. Laboratory control sample(s) should be analyzed with each batch of samples
 - 12.1.2 The laboratory control samples must be spiked with each analyte of interest at the project-specific action level or, when lacking projectspecific action levels, at approximately mid-point of the linear dynamic range.
- 12.2 Laboratory Fortified Blank (LFB) also known as the Laboratory Control Sample.
- 12.3 Method Blank
- 12.4 Laboratory Reagent Blank (LRB) An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

13.0 REFERENCES

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- 13.13 Method 200.8, Revision 5.4, 1998.
- 13.14 SW-846, Method 6020A Revision 1, 2007
- 13.15 SW-846, Method 8000C Revision 3, 2003

14.0 APPROVAL & ISSUE:

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

Analyst	Date
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Andrew Ball, QA Officer	Date
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Maya V. Murshak, Technical Director	Date
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15.0 TABLES/FIGURES/APPENDIXES

Table 1. List of elements analyzed.

Table 2. Standard preparation for all elements except Ca, Mg, K, Na.

Table 3. Standard preparation for Ca, Mg, K, Na.

Table 4. ICS Components and Concentration.

Table 5a & 5b. Recommended analytical isotopes and additional masses to be monitored.

Table 6. Quality Control Items, Frequency, and Corrective Action.

Appendix 1. ICP/MS Standards Prep Log

Appendix 2. ICP/MS Initial Calibration Verification (ICV) Prep Log

Appendix 3. Metals Digestion Log

Figure 1. MS/MSD Corrective Action Flow Chart

Table 1. List of elements analyzed.

Element	Symbol	CAS#	Reporting Limits		Method Reference		
			mg/L	mg/kg	6020	200.8	6020A
Aluminum	Al	7429-90-5	0.05	0.5	X	X	X
Antimony	Sb	7440-36-0	0.002	0.3	X	X	X
Arsenic	As	7440-38-2	0.001	0.1	X	X	X
Barium	Ba	7440-39-3	0.01	1.0	X	X	X
Beryllium	Be	7440-39-3	0.001	0.50	X	X	X
Boron	B	7440-42-8	0.01	1.0			
Cadmium	Cd	7440-43-9	0.0005	0.2	X	X	X
Calcium	Ca	7440-70-2	0.05	10.0	X		X
Chromium	Cr	7440-47-3	0.005	2.0	X	X	X
Cobalt	Co	7440-48-4	0.01	0.5	X	X	X
Copper	Cu	7440-50-8	0.004	1.0	X	X	X
Iron	Fe	7439-89-6	0.1	1.0	X		X
Lead	Pb	7439-92-1	0.003	1.0	X	X	X
Lithium	Li	7439-93-2	0.01	1.0			
Magnesium	Mg	7439-95-4	1.0	4.0	X		X
Manganese	Mn	7439-96-5	0.02	1.0	X	X	X
Molybdenum	Mo	7439-98-7	0.005	0.50		X	
Nickel	Ni	7440-02-0	0.005	1.0	X	X	X
Potassium	K	7440-09-7	1.0	5.0	X		X
Selenium	Se	7782-49-2	0.005	0.2	X	X	X
Silver	Ag	7440-22-4	0.0002	0.1	X	X	X
Sodium	Na	7440-23-5	0.05	10.0	X		X
Strontium	Sr	7440-24-6	0.005	0.50			
Tin	Sn	7440-31-5	0.02	1.0			
Titanium	Ti	7440-32-6	0.005	1.0			
Thallium	Tl	7440-28-0	0.001	0.50	X	X	X
Vanadium	V	7440-62-2	0.004	1.0	X	X	X
Zinc	Zn	7440-66-6	0.01	1.0	X	X	X

Table 2. Standard preparation for all elements except Ca, Mg, K, Na (metals).

Standards	Volume Working Stock Solution	Internal Standard 5.0 ppm	HNO ₃	Final Volume
0.50 ppm	5.00 ml WS1	2 ml	2 ml	100 ml
0.20 ppm	2.00 ml WS1	2 ml	2 ml	100 ml
0.10 ppm	1.00 ml WS1	2 ml	2 ml	100 ml
0.05 ppm	0.50 ml WS1	2 ml	2 ml	100 ml
0.02 ppm	20.0 ml WS2	2 ml	2 ml	100 ml
0.01 ppm	10.0 ml WS2	2 ml	2 ml	100 ml
0.005 ppm	5.00 ml WS2	2 ml	2 ml	100 ml
0.002 ppm	2.00 ml WS2	2 ml	2 ml	100 ml
0.0005 ppm	0.50 ml WS2	2 ml	2 ml	100 ml
0.0001 ppm	0.10 ml WS2	2 ml	2 ml	100 ml
0.00 ppm	0.00 ml WS2	2 ml	2 ml	100 ml

Note:

- Inorganic Stock Solution IV-7 + IV-19 (100 ppm)
- WS1 Working Stock Solution 1
10 ml IV-7 + 10 ml IV-19 + 2 ml HNO₃; Bring to a final volume of 100 ml = 10 ppm
- WS2 Working Stock Solution 2
1ml of WS1 to a final volume of 100 ml = 0.100 ppm
- Spiking Solution
50 ml of WS1 to a final volume of 100 ml = 5.0 ppm

Table 3. Standard preparation for Ca, Mg, K, Na (minerals).

Standards ppm	Volume of Working Stock	Source and Lot # of Working Stock (100ppm)	Internal Standard 5.0 ppm	HNO ₃	Final Volume
0.20	0.2	High Purity – 620719	2 ml	2 ml	100 ml
0.50	0.5	High Purity - 620719	2 ml	2 ml	100 ml
1.0	1.0	High Purity - 620719	2 ml	2 ml	100 ml
2.0	2.0	High Purity - 620719	2 ml	2 ml	100 ml
5.0	5.0	High Purity - 620719	2 ml	2 ml	100 ml
10.0	10.0	High Purity - 620719	2 ml	2 ml	100 ml
ICV- 5.0	5.0	Spex – 5-59JB	2 ml	2 ml	100 ml

Table 4. ICS Components and Concentration.

Solution Component	ICS-A (ppm)	ICS-AB (ppm)
Al	100.0	100.0
Ca	100.0	100.0
Fe	100.0	100.0
Mg	100.0	100.0
Na	100.0	100.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.020
Cd	0.0	0.020
Cr	0.0	0.020
Co	0.0	0.020
Cu	0.0	0.020
Mn	0.0	0.020
Ni	0.0	0.020
Ag	0.0	0.020
Zn	0.0	0.020

Table 5a. Recommended analytical isotopes (underlined) and additional masses to be monitored.

Mass	Element	I.S. Used	Elemental Correction	Potential interferences
<u>19</u>	K	Sc, Rh		
<u>23</u>	Na	Sc, Rh		
<u>24</u>	Mg	Sc, Rh		
43	Ca	Sc, Rh		
<u>44</u>	Ca	Sc, Rh	(-0.0271)(⁸⁸ C)	Sr ⁺⁺

- Notes:**
- † Recommended for PE instrument.
 - ‡ Recommended for HP instrument.
 - C = Counts at specified mass.
 - When the concentration of Na in the samples is high, the ionization of Sc is suppressed leading to positive bias of the results, therefore Rh must be used as the internal standard, even if more than 50 amu removed from the element of interest.

Table 5b. Recommended analytical isotopes (underlined> and additional masses to be monitored.

Mass	Element	I.S. Used	Elemental Correction	Potential interferences
6	Li	I.S.	-(0.0813)(⁷ C)	
<u>7</u>	Li	⁶ Li, Sc		
<u>9</u>	Be	⁶ Li, Sc		
10	B	⁶ Li, Sc		
<u>11</u>	B	⁶ Li, Sc		
<u>27</u>	Al	⁶ Li, Sc		
45	Sc	I.S.		CO ₂ H ⁺
47	Ti	⁶ Li, Sc		
<u>49</u>	Ti	⁶ Li, Sc		
<u>51</u>	V	⁶ Li, Sc	-(3.127)(⁵³ C)+(0.352)(⁵² C)	³⁵ ClO ⁺ , ³⁴ SOH ⁺
<u>52</u> [†]	Cr	Sc, Y, Rh		ArC ⁺ , ArO ⁺ , ³⁵ ClHO ⁺
<u>53</u> [‡]	Cr	Sc, Y, Rh		³⁷ ClHO ⁺
<u>54</u> [†]	Fe	Sc, Y, Rh	-(0.0284)(⁵² C)	
<u>55</u>	Mn	Sc, Y, Rh		ArNH ⁺
56	Fe	Sc, Y, Rh		
<u>57</u> [†]	Fe	Sc, Y, Rh		
<u>58</u> [†]	Ni	Sc, Y, Rh		
<u>59</u>	Co	Sc, Y, Rh		
<u>60</u>	Ni	Sc, Y, Rh		
62	Ni	Sc, Y, Rh		TiO
<u>63</u> [†]	Cu	Sc, Y, Rh		³¹ PO ₂ ⁺ , ⁴⁰ ArNa ⁺ , TiO
<u>65</u> [†]	Cu	Sc, Y, Rh		TiO
<u>66</u>	Zn	Sc, Y, Rh		TiO
68	Zn	Sc, Y, Rh		
<u>75</u>	As	Y, Rh	-(3.132)(⁷⁷ C)+(2.736)(⁸³ C)	⁴⁰ Ar ³⁵ Cl ⁺
76	⁴⁰ Ar ³⁶ Ar ⁺	Y, Rh		⁴⁰ Ar ³⁷ Cl ⁺
77	Se	Y, Rh		
<u>78</u> [†]	Se	Y, Rh	-(0.1869)(⁷⁶ C) [‡]	⁴⁰ Ar ³⁸ Ar ⁺
<u>82</u> [†]	Se	Y, Rh		⁸¹ BrH ⁺
83	Kr	Y, Rh		
<u>88</u>	Sr	Y, Rh		
89	Y	I.S.		
90	Zr	Y, Rh		
<u>95</u>	Mo	Y, Rh		⁷⁹ BrO ⁺
98	Mo	Y, Rh	-(0.146)(⁹⁹ C)	⁷⁹ BrHO ⁺
99	Ru	Y, Rh		
103	Rh	I.S.		
105	Pd	Rh		
106	Pd, Cd	Rh		ZrO,
<u>107</u>	Ag	Rh		ZrO
108	MoO	Rh		ZrO, MoO
109	Ag	Rh		ZrO, MoO
<u>111</u>	Cd	Rh		ZrO, MoO
112	Cd	Rh	-(0.040)(¹¹⁸ C)	ZrO, MoO
<u>114</u>	Cd	Rh	-(0.0269)(¹¹⁸ C)	MoO
<u>118</u>	Sn	Rh		
119	Sn	Rh		
120	Sn	Rh	-(0.0127)(¹²⁵ C)	
<u>121</u>	Sb	Rh	-(0.124)(¹²⁵ C)	⁴⁰ Ar ⁸¹ Br ⁺
123	Sb	Rh		
125	Te	Rh		
<u>137</u>	Ba	Rh		
138	Ba	Rh	-(8.91E-04)(¹³⁹ C)-(2.82E-04)(¹⁴⁰ C)	
139	La	Rh		
140	Ce	Rh		
185	Re	I.S.		
203	Tl	Re		
<u>205</u>	Tl	Re		
206	Pb	Re		
207	Pb	Re		
<u>208</u>	Pb	Re	+(1.0)(²⁰⁶ C)+(1.0)(²⁰⁷ C)	

Notes: • † Recommended for the PE instrument.
• ‡ Recommended for the HP instrument.

Table 6. Summary of Quality Control Items, Frequency, and Corrective Action.*

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tuning	After warm-up Every 12 hours	Manufacturer specifications	Check operating parameters, clean cones, replace malfunctioning components if necessary. Reevaluate the tuning.
Calibration Curve	Once a day and as necessary	$R \geq 0.998$ The lowest non-zero calibration point must be at or below reporting limit	Remove allowed points keeping minimum of 3 non-zero points, replace calibration standards if needed and recalibrate instrument.
ICV	After every calibration	90-110%	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, and recalibrate the instrument.
ICB	After every ICV	Less than the lower limit of quantitation for every target element.	Prepare fresh calibration blank and/or increase the rinse time between analyses; reanalyze ICB; if within limits, continue the run; if still outside limits, determine the source of the problem, make the necessary corrections, and start from the beginning with a new calibration.
LLICV	After initial calibration	70-130% Not required for 200.8	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, prepare a fresh calibration blank, and recalibrate the instrument.
CCV	After Every 10 sample or less	90-110%	Recalibrate the instrument. Follow method specific requirements (6020, 6020A or 200.8) as to what data prior to the CCV can be used.
CCB	After Every 10 sample or less	Less than the lower limit of quantitation for every target element.	Prepare fresh calibration blank; reanalyze CCB; if within limits, continue the run; if still outside limits, eliminate the source of the contamination, clean the sample introduction system if necessary, and recalibrate the instrument. Reanalyze all samples from the last good CCB.
LCS	Every batch of 20 samples or less	85-115%	Re-digest the entire sample batch and reanalyze.
LRB (MB)	Every batch of 20 samples or less	<RL/Dilution factor	Re-digest the entire sample batch and reanalyze.
Dp	Every 10 water samples or every 20 soil samples	0-20%	If all other QC acceptable continue the run; sample result must be flagged; otherwise recalibrate instrument and reanalyze samples.
MS	Every 10 water samples or every 20 soil samples, prior to digestion	75-125%	The sample is spiked and re-analyzed according to Figure 1.
MSD [†]	Every 10 water samples or every 20 soil samples, prior to digestion	0-20%	Same as for duplicate.
Dil [‡]	Once with every batch of 20 samples or less	0-10% Not required for 200.8	If concentration analyzed >100 x MDL, flag data for possible matrix interference.
ICS-A [‡]	Every 12 hours	<RL for water samples Not required for 200.8	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument. Re-analyze samples associated with the failed ICS.
ICS-AB [‡]	Every 12 hours	70-135% Not required for 200.8	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument. Re-analyze samples associated with the failed ICS.
IS Samples	With every sample	70-125%	Verify matrix interference by ruling out instrument drift by unacceptable IS recoveries in standards. Dilute 4+1 and reanalyze. Repeat until inside control limits.
IS QC Samples	With every QC Sample	80-120% for ICV/ICB and CCV/CCB	For CCV/CCB's recalibrate the instrument and reanalyze the affected samples.

NOTE:

- *This is a summary table for more information see Sections 8.4 to 8.10
- RL = Reporting Limit.
- Dil = Dilution Test.
- † MSD optional instead of duplicate sample.
- ‡ When Method 6020 & 6020A referenced in the analytical report.
- IS = Internal Standard

ICP/MS STANDARDS PREP LOG

[illegible]

Exp. Date: _____

ICP/MS INITIAL CALIBRATION VERIFICATION (ICV) PREP LOG

[illegible]**Expiration Date**

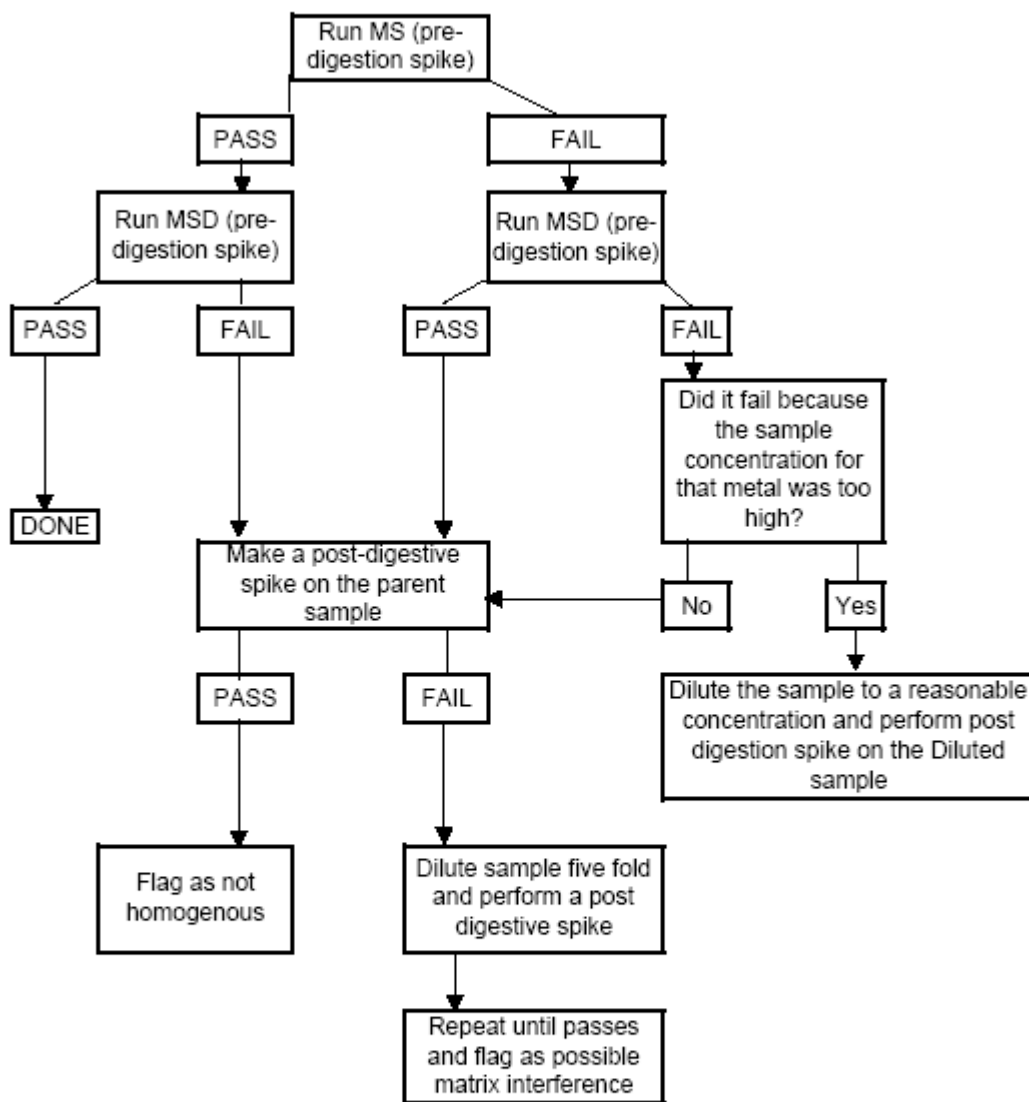
METALS DIGESTION

DATE _____
ANALYST _____

[illegible]

3) HNO_3 Lot # 068109

FIGURE 1 MS/MSD CORRECTIVE ACTION FLOW CHART



1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub- $\mu\text{g/L}$ concentrations of a large number of elements in water samples and in waste extracts or digests. When dissolved constituents are required, samples are filtered through 0.45 μm membrane filters and acid-preserved prior to analysis. No digestion is needed prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is performed for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are needed. Acid digestion is also needed prior to analysis to dissolve elements in drinking water samples with turbidity <1 NTU. This SOP follows the guidelines of the EPA Methods 200.8 and 6020.

1.2 The metals that can be determined by using this SOP are listed bellow. Elements specific to each method (*i.e.* 6020, 6020A, 200.8) and reporting limits are listed in Table 1.

<u>Metal (Symbol)</u>	<u>CAS#:</u>
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Boron (B)	7440-42-8
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-95-4
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Strontium (Sr)	7440-24-6
Tin (Sn)	7440-31-5
Titanium (Ti)	7440-32-6
Thallium (Tl)	7440-28-0
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

1.3 If this SOP is used to determine any analyte not listed in the table above, it is the responsibility of the analyst to demonstrate the accuracy and precision of the Method in the samples to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality.

1.4 Use of this method is restricted to analysts who are knowledgeable in the recognition and in the correction of spectral, chemical and physical interferences in ICP-MS.

2.0 SUMMARY OF METHOD

- 2.1 Prior to analysis, samples which require total ("acid-leachable") values are digested using appropriate sample digestion procedures (see SOP 3015dig and 3051dig).
- 2.2 This SOP describes the measurement of ions produced by radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios, and quantified with a channel electron multiplier. Potential interference from isobaric elements and polyatomic ions are corrected for by the use of elemental interference equations based on natural isotope abundance. Interference corrections include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix. Instrument drift and matrix induced signal suppressions and enhancements are compensated for by the use of internal standardization.

3.0 INTERFERENCES

There are three fundamentally different sources of interference in ICP-MS: spectroscopic interferences, physical, and memory interferences.

- 3.1 **Spectroscopic Interferences** are interferences caused by the presence of compounds or elements entering the mass spectrometer which have the same nominal mass to charge (m/z) ratio as the analyte elements. They can be isobaric elemental and isobaric molecular interferences (polyatomic, refractory oxide, and doubly charged ions).

- 3.1.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z) as the analyte element. These can be managed by the selection of an alternate isotope for analysis or by the use of elemental interference equations. These equations use the naturally occurring isotope ratios of most elements to estimate and allow for the subtraction of isobaric interferences. An example of an elemental isobaric interference is ^{40}Ar on ^{40}Ca . In this case, the use of ^{43}Ca or ^{44}Ca is recommended. The appropriate elemental interference equations are incorporated in the methods (or parameter) used for calibration and data acquisition.

- 3.1.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that affect ICP-MS determinations have been identified. Examples include ArCl^+ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundance, the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting statistics.

- 3.1.2.1 Example for As is as follows: Because the ^{35}Cl natural abundance of 75.77 % is 3.13 times the ^{37}Cl abundance of 24.23 %, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}\text{Ar}^{37}\text{Cl}^+$ contribution at m/z 75 is a negligible 0.06 % of the $^{40}\text{Ar}^{35}\text{Cl}^+$ signal): Corrected arsenic signal (using natural isotopes abundance for coefficient approximations) = (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), (where the final term adjusts for any selenium contribution at 77 m/z).

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}\text{Se}^+$, (e.g., $^{81}\text{BrH}^+$ from bromine wastes⁶).

- 3.1.2.2 Example for Cd is as follows: corrected cadmium signal (using natural isotopes abundance for coefficient approximations) = (m/z 114 signal) - (0.027)(m/z 118

signal) - (1.63)(m/z 108 signal), (where last 2 terms adjust for any tin or MoO⁺ contributions at m/z 114).

NOTE: Cadmium values will be biased low by this type of equation when ⁹²ZrO⁺ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct (⁹⁴ZrOH⁺) and indirect (⁹⁰ZrO⁺) additive interferences when Zr is present.

NOTE: Since there is a certain degree of uncertainty as to which equation is better to use, and in what cases, it is up to the analyst to determine how the interference will be corrected, upon the evaluation of data. It is suggested that the elemental isobaric interference equations be included in all methods (parameters) from the beginning, but potential polyatomic species (masses) that could interfere be only monitored (except for ⁴⁰Ar³⁵Cl⁺ on As). When species monitored indicate that an isobaric molecular interference is present, the equations can be adjusted to correct for such interference, and data be reprocessed to produce an interference free summary report. Generally, an interference is easy to spot when multiple isotopes of an element show different results. Since the interference is additive, the use of the isotope with the lowest result is suggested for data reporting, providing that all other QC criteria are met.

3.1.3 Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. Wing overlap interference may occur when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized, and the spectrometer resolution adjusted to minimize them. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require matrix separation, or analysis using another verified and documented isotope.

3.2 **Physical Interferences** are associated with the physical processes, which govern the transport of sample into the plasma, sample conversion process within the plasma and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the samples and calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g. viscosity effects), at the point of aerosol formation and transport to the plasma (e.g. surface tension effects), during the atomization and ionization process within the plasma itself, or during the transfer of ions through the interface and mass spectrometer (space charge effects). To minimize some of these effects, acid composition and concentration should be matched for all standards, blanks, and samples. Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards should ideally display similar analytical behavior to the elements being determined. Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ⁶Li, ⁴⁵Sc, ⁸⁹Y, ¹⁰³Rh, ¹¹⁵In, ¹⁵⁹Tb, ¹⁶⁹Ho, ¹⁸⁵Re, and ²⁰⁹Bi.

3.3 **Memory Interferences** result when elements in a previous sample contribute to signals measured in a subsequent sample. Memory effects can result from the deposition of sample on various components of the sample introduction system, including sample and peristaltic pump tubing, spray chamber, torch, and interface cones. The site(s) where deposition may occur is dependent on the sample and may need to be minimized through the use of a rinse blank between samples. Routine maintenance (cleaning and/or replacement) of sample introduction components is necessary for long-term minimization of memory effects. The possibility of memory interferences within an analytical run should be recognized and suitable rinse times should be used to reduce them. Memory effects are evaluated by using a minimum of three replicate integrations for data acquisition. High relative standard deviation (%RSD) of the three replicates caused by a consecutive drop in signal intensity is indicative of carryover from the previous sample. If a memory interference is suspected, the sample should be reanalyzed after analysis of a blank indicates that the carryover has been eliminated.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled plasma-mass spectrometers:

4.1.1 **Perkin Elmer (PE) Elan 9000 ICP-MS:**

- Windows XP Operating System
- Elan 3.0 Software
- Cetac Asx510 Autosampler

4.1.2 **Hewlett-Packard (HP) 4500 ICP-MS:**

- Windows 95 operating system.
- Chem Station Software.
- Cetac ASX150 Autosampler.

4.2 Argon gas supply: liquid argon cylinders.

4.3 Analytical balance, 510g capacity, minimum accuracy ± 0.001 g.

4.4 Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.

4.5 Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 μ l to 5,000 μ l.

4.6 Disposable Pasteur pipettes.

4.7 Polypropylene vessels, 50 mL.

4.8 Plastic cups to support minimum of 200 ml.

4.9 Plastic bottles.

5.0 REAGENTS

5.1 Nitric Acid (HNO_3), concentrated, Trace Metal Grade. Acids used in the preparation of standards and for sample processing must be of high purity. Trace metal grade (also known as re-distilled) acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at 2% (v/v) or less in the solution to be analyzed is required for ICP-MS, in order to minimize damage to the interface.

5.2 Hydrochloric Acid (HCl), concentrated, Trace metal Grade. Several polyatomic ion interferences result when HCl is used. However, its use is recommended to maintain stability in solutions containing high concentrations of antimony and silver. When used, corrections for the chloride polyatomic ion interference must be applied to all data.

5.3 Reagent water (Deionized water): All references to reagent water in the method refer to ASTM Type I water (ASTM D1193), unless otherwise specified.

5.4 Internal Standard stock solutions:

5.4.1 Lithium 6, 1000 μ g/ml stock solution.

5.4.2 Scandium, 1000 μ g/ml stock solution.

5.4.3 Yttrium, 1000 μ g/ml stock solution.

5.4.4 Rhodium, 1000 μ g/ml stock solution.

5.4.5 Rhenium, 1000 μ g/ml stock solution.

5.4.6 Internal Standard working solution (**IS-WS**): From the above stock solution, 5 g of each is transferred to a 1000 ml plastic bottle, along with 20 ml of concentrated HNO_3 and brought to a final volume of 1000 ml (by weight). The concentration in the flask will be approximately 5.0 μ g/ml. This represents the internal standards working solution from which 1 ml (for a 50 ml final volume) will be added to all calibration standards and blanks. This will provide a 0.10 ppm of internal standard concentration in all calibration standards, similar to analytical samples.

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor.

5.5 Multielement standard stock solution from three different vendors:

- 5.5.1 Inorganic Venture (IV), 100mg/L each of Ag, Al, B, Ba, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, Tl, V, Zn.. This solution is used for the preparation of standards.
- 5.5.2 High Purity Standards (HM), 100 µg/ml each of Ca, Mg, K, Na. This solution is used for the preparation of the calibration standards and for the minerals standard.
- 5.5.3 SPEX Industries (S), 100 µg/ml each of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, K, Se, Si, Ag, Na, Sr, Sn, Ti, Tl, V, Zn. This solution is used for the preparation of the initial calibration verification (ICV) standards.
- 5.5.2 Environmental Resource Associates (ERA), concentration varies by lot number and element but contains all of the following Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Ag, Zn, V, Th, S. This solution is used as a third source of verification

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor. See Appendix 1 for standard preparation.

- 5.6 Multielement calibration standard solutions are prepared by diluting the stock standard solutions to levels in the linear range for the instrument in a solvent consisting of 2% (v/v) HNO₃ in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. The calibration standards are kept in plastic bottles, and prepared every two weeks or as needed. They must be verified using a quality control standard (ICV). Table 2 and Table 3 can be used as guidance, when preparing standards.
- 5.7 Blanks: Three types of blanks are required for the analysis. The calibration blank (std-0.00) is used in establishing the calibration curve. The preparation blank (LRB) is used to monitor possible contamination resulting from the sample preparation procedure. The rinse blank (also called optional rinse or autosampler wash) is used to flush the system between all samples and standards.
 - 5.7.1 The calibration blank (std-0.00) and the continuing calibration blank (CCB) consists of the same concentration(s) of the same acid(s) used to prepare the calibration standards, along with the appropriate concentration of internal standard.
 - 5.7.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.
 - 5.7.3 The rinse blank consists of 2% HNO₃ (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.
- 5.8 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interference such as ³⁵Cl¹⁶O⁺ on ⁵¹V⁺ and ⁴⁰Ar³⁵Cl⁺ on ⁷⁵As⁺. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

- 5.8.1 Interference check stock solution A, containing 1000 µg/ml each of Al, Ca, Fe, Mg, Na, P, K, S, 2000 µg/ml of C, 10000 µg/ml of Cl, and 20.0 µg/ml each of Mo and Ti. The ICS-A solution is prepared by weighing 10.0 g of the stock solution in a plastic cup, addition of 2 ml IS-WS, 2ml HNO₃, and dilution to 100 g on the scale with reagent water.
 - 5.8.2 Interference check stock solution AB, containing 2.0 µg/ml each of As, Cd, Cr, Co, Cu, Mn, Ni, Ag, and Zn. The ICS-AB solution is prepared by weighing 1.00 g of the stock solution in a plastic cup, addition of 2 ml IS-WS, 2ml HNO₃, and dilution to 100 g on the scale with reagent water.
 - 5.8.3 The final concentration of the elements in ICS-A and ICS-AB is listed in Table 5. These solutions are prepared fresh every two weeks or as needed.
 - 5.9 The quality control standard is the initial calibration verification solution (ICV), which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard from a source different from those used in the standards for instrument calibration.
 - 5.10 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Section 7.5). This solution is also used to verify that the instrument has reached thermal stability (See Section 7.4).
 - 5.10.1 Tuning solution for HP 4500 ICP-MS: 10 µg/ml each of Li, Y, Ce, and Tl. Take 1.00 g of this solution in a plastic bottle, add 20 ml HNO₃, and dilute to 1000 g on the scale with reagent water (or add 979 g reagent water to the bottle with standard and acid). This will result in a 10.0 ppb solution of the above elements, used to tune the instrument according to the manufacturer instructions.
 - 5.10.2 Tuning solution for PE Elan 9000 Tune Solution 6020-Li Co In Tl (10 ppb) Tune Solution 200.8- Be Mg Co In Pb (10ppb) This is used to tune the instrument according to the manufacturer instructions.
 - 5.11 Drinking water working standards are prepared every two weeks
- 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING
- 6.1 All samples are collected in appropriate containers. For water samples, the samples are collected in HNO₃ pre-preserved plastic container (approximately 125 ml volume), and are acidified to pH of <2.
 - 6.2 Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples should be refrigerated upon receipt and analyzed as soon as possible.
 - 6.3 Holding times for metals are 6 months from the date of sampling.

7.0 PROCEDURE

- 7.1 Solubilization and digestion procedures are presented in the Sample Preparation SOP's (e.g., 3015dig, 3051dig).
- 7.2 Initiate appropriate operating configuration of the instrument's computer according to the instrument manufacturer's instructions.
- 7.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions (Table 4).

- 7.4 Operating conditions: The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (Section 5.10.1 and 5.10.2).
- 7.5 Tune the instrument according to the instrument manufacturer's instructions. For drinking water samples the tuning requirements are listed in the 200.8 method. The tuning should include beryllium, magnesium, cobalt, indium, and lead. Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria that must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be within 0.5-0.9 amu full width at 10 percent peak height.

NOTE: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

- 7.6 Calibrate the instrument for the analytes of interest (recommended isotopes for the elements in Section 1.2 are provided in Table 6a and Table 6b), using the calibration blank and at least a single initial calibration standard according to the instrument manufacturer's procedure. Table 2 and Table 3 (Section 5.6) provides information as to what calibration standards to use. Flush the system with the rinse blank (Section 5.7.3) between each standard solution. Use the average of at least three integrations for both calibration and sample analyses.
- 7.7 All masses that could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are listed in Table 6a, and Table 6b).
- 7.8 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the calibration verification solution (ICV, Section 5.9). When measurements exceed $\pm 10\%$ of the accepted value, the analyses must be terminated, the problem corrected, the instrument re-calibrated, and the new calibration verified. During the course of an analytical run, the instrument may be "re-sloped" or re-calibrated to correct for instrument drift. A re-calibration must then be followed immediately by a new analysis of a ICV and ICB before any further samples may be analyzed. Corrective actions for specific situations are summarized in Table 7.
- 7.9 An optional Blank Spike (BS) of low concentration can be used to verify the linearity of the calibration curve near the lower end. When such standard is used, recalibrate the instrument if the recovery of the BS is outside 70-130% of true concentration.
- 7.10 Flush the system with the rinse blank solution (Section 5.7.3) until the signal levels return to the method's levels of quantitation (usually about 30 seconds) before the analysis of each sample. Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (CCV), and the continuing calibration blank (CCB) at a frequency of at least once every 10 analytical samples.
- 7.11 Dilute and reanalyze samples that are more concentrated than the linear range (LDR Section 8.2.2.) for an analyte or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 7.6 and 7.8).
- 7.12 Calculations: The quantitative values shall be reported in appropriate units, such as milligrams per liter (mg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples.
- 7.12.1 The appropriate dilution factor (DF) resulted from sample preparation (see 3015dig and 3051B SOP's) is entered in the data system for each sample at the time of programming the

sequence to be analyzed. If additional dilutions are performed, the appropriate corrections must be applied to the dilution factor.

- 7.12.2 Generally, for solid samples, DF includes the correction necessary for the determination of a dry weight result. If this is not the case or if a dry weight result is requested at a later time, calculate results for solids on a dry-weight basis as follows:

- (1) A separate determination of percent solids must be performed.
- (2) A new DF can be calculated, based on the original wet weight of the sample (from the preparation log) and the percent total solids. The sequence is updated with the new DF, data reprocessed, and a new quantitation report is generated by the data system.
- (3) Manual calculation of the dry weight concentration (DWC) by the formula:

$$DWC \text{ (mg / kg)} = \frac{CxV}{WxS}$$

Where, C = Digest Concentration (mg/L).

V = Final volume in liters after sample preparation.

W = Weight in kg of wet sample.

S = (% Total Solids)/100.

- 7.12.3 Calculations performed by the data system include appropriate interference corrections, internal-standard normalization, and the summation of signals at 206, 207 and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

8.0 QUALITY CONTROL

- 8.1 All quality control data should be maintained and be available for easy reference or inspection.

- 8.2 Initial Demonstration of Performance.

- 8.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear calibration ranges) and laboratory performance (determination of method detection limits) prior to analyses conducted by this method.

- 8.2.2 Linear calibration ranges: Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The linear calibration range, which may be used for the analysis of samples, should be judged by the analyst from the resulting data. The upper LDR is defined as the maximum concentration for which the measured concentration is within $\pm 10\%$ of the true value. Determined sample analyte concentrations that are greater than the upper LDR limit must be diluted and reanalyzed. The LDR should be verified whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

- 8.2.3 Method detection limits (MDL) should be established for all analytes, using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit. To determine MDL values, take seven 7 replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

Where: t = student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicates);

S = standard deviation for the replicate analyses.

MDL's should be determined annually, when a new operator begins work or whenever, in the judgement of the analyst, a change in the instrument hardware or operating conditions would dictate they be redetermined.

- 8.3 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification or the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon, and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. If an interference source is present, and can not be corrected, the sample elements impacted must be flagged. When correction equations are used, all QC criteria must also be met.
- 8.4 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall outside limits as compared with the first calibration standard (Calibration Blank or std-0.00), the following procedure is followed. The sample must be diluted at least fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal-standard intensities fall within the prescribed window. The intensity levels of the internal standards for the ICV/ICB, CCV/CCB, LCS/LRB must also be within the specified acceptance limits (refer to Section 8.9.1.3 and 8.9.2.4 for limits). If they are not, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.
- 8.5 Check the instrument calibration by analyzing appropriate quality control solutions as follows:
- 8.5.1 Check instrument calibration by analyzing the initial calibration verification solution (ICV) and the initial calibration blank (ICB).
- 8.5.2 Verify calibration at a frequency of every 10 analytical samples with the CCV standard and the continuing calibration blank (CCB). These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample.
- 8.5.3 The results of the ICV and CCV must agree within $\pm 10\%$ of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument.
- 8.5.4 The results of the ICB and CCB's must be less than the current RDL for each element or less than the reporting limits for sample, whichever is greater. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed.
- 8.6 A Laboratory Control Sample (LCS) should be analyzed for each analyte using the same sample preparations, analytical methods, and QA/QC procedures employed for the test samples. One LCS should be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less. The recovery limits for the LCS are 85-115% of the true value (stated in the preparation log).
- 8.7 Analyze one matrix spike (MS) sample for every 10 analytical water samples or every 20 analytical soil samples. For majority of the elements, the aqueous samples are spiked at levels similar to the LCS (0.05 ppm in the analysis solution). For solid samples, the concentration added is approximately 20 mg/Kg equivalent (0.10 ppm in the analysis solution). The acceptable limits for performance are summarized in Section 8.10.

- 8.7.1 Calculate the percent recovery of each analyte, corrected for background concentrations measured in the unfortified (original) sample. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{S} \times 100$$

where: R = percent recovery.

C_s = spiked sample concentration.

C = sample background concentration.

S = concentration equivalent of analyte added to fortify the sample.

- 8.8 Analyze one matrix duplicate (Dp) sample for every 10 water samples or every 20 soil samples. In some cases, a matrix spike duplicate (MSD) can be used instead of the matrix duplicate, especially if the analytes in the sample are of low concentration. A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the MDL. If this limit is exceeded and laboratory performance for that analyte is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the problem encountered is judged to be matrix related. The data user should be informed that the result for that analyte is suspect due to the heterogeneous nature of the sample. If the performance of the laboratory is not in control (ICV/ICB, CCV/CCB, and LCS/LRB outside the limits), the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition for that analyte must be reanalyzed.

- 8.8.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} \times 100$$

where: RPD = relative percent difference.

D_1 = first sample value.

D_2 = second sample value (duplicate).

- 8.9 The Quality Control requirements and limits vary slightly, based upon the method referenced in the analytical report (i.e. 6020 vs. 200.8). For both methods, the calibration is verified by the analysis of ICV/ICB and CCV/CCB. Recalibration is required when either one falls outside the limits. The performance of the method is evaluated by the analysis of the LCS/LRB pair for every batch of 20 samples, and MS/MSD/Dp for every 10 samples.

- 8.9.1 Method 200.8 specific requirements:

8.9.1.1 When the recovery for ICV/CCV falls outside $\pm 10\%$ terminate the analysis and recalibrate the instrument. If the last CCV was within 15% of the true concentration, the results for the samples are still acceptable. If this is not the case, the only acceptable results are the once corresponding to samples analyzed before the last CCV that was within 15% of the true concentration. All other samples are to be analyzed again, after recalibration of the instrument.

8.9.1.2 The recovery limits for MS samples are 70-130%. If the recovery of any analyte falls outside the designated range and the laboratory performance is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the recovery problem encountered with the spiked sample is judged to be matrix related, not system related. The data user should be informed that the result for the analyte in the unspiked sample is suspect due to an uncorrected matrix effect. Recovery is not required if the concentration of the analyte added is less than 30% of the concentration of the analyte in the original sample.

8.9.1.3 The absolute response of any one internal standard must not deviate by more than 60 to 125% of the original response in the first calibration standard (Calibration Blank or std-0.00). If deviations greater than these are observed flush the instrument with rinse blank, then analyze a CCB. If the responses of the internal standards are now within the limit proceed with sample dilution as described in Section 8.4. If the responses of the internal standards are not within the limit, terminate the analysis, recalibrate the instrument, and reanalyze the samples from the last CCB with acceptable internal standard recoveries.

8.9.2 Method 6020 specific requirements:

8.9.2.1 When the recovery for ICV/CCV falls outside $\pm 10\%$ terminate the analysis and recalibrate the instrument. The samples from the last CCV that was within limits are to be re-analyzed, after recalibration of the instrument.

8.9.2.2 The MS is represented by a spiked sample, before digestion, and a Post-Digestion Spike, if the recovery of the regular spike fails to meet QC criteria. An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the original sample must be diluted to compensate for the matrix effect, and reanalyzed, after a new post-digestion spike is added. The same recovery limits apply to the spiked dilution.

8.9.2.3 The MSD is represented by a spiked duplicate sample, before digestion, and a Post-Digestion Spike, if the recovery of the regular duplicate spike fails to meet QC criteria. The evaluation of the MSD is similar to the evaluation of the duplicate analysis described in Section 8.8.

8.9.2.4 When the intensity of any internal standard in the sample to falls outside 30-120% of the intensity of that internal standard in the initial calibration standard (Calibration Blank or std-0.00), follow the procedure described in Section 8.4. The intensity levels of the internal standards for the ICV/ICB and CCV/CCB must agree within ± 20 percent of the intensity level of the initial calibration standard (Calibration Blank or std-0.00). If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

8.9.2.5 Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 x MDL), an analysis of a fivefold (1+4) dilution must agree within $\pm 10\%$ of the original determination. If not, an interference effect must be suspected, and the results flagged. One dilution test must be included with every batch of twenty samples.

8.9.2.6 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions ICS-A and ICS-AB. The recovery of the elements of interest in ISC-AB (listed in Table 5 at a concentration of 0.02 ppm) should be between 70-135%.

8.10 Summary of the QC requirements and performance acceptance limits are shown in the following table:

QC Type	Method 6020 (%)	Method 200.8 (%)
ICV	90-110	90-110
BS	70-130	70-130
CCV	90-110	90-110*

Dp	0-20	0-20
MS	75-125	70-130
MSD	0-20	0-20
ICS-AB	70-135	n.a.
Internal Standard	80-120 for CCV/CCB 30-120 for samples	80-120 for CCV/CCB 60-125 for samples

*NOTE: *Sample results still acceptable if CCV between 85-115%.*

9.0 METHOD PERFORMANCE

- 9.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.
- 9.2 Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.
- 9.3 In an EPA multi-laboratory study, laboratories applied the ICP-MS technique to both aqueous and solid samples. The results are listed at the end of methods 200.8 and 6020.

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11.0 APPROVAL & ISSUE:

Paul Roettger, Senior Analyst

Date

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Date

12.0 LIST OF TABLES

Table 1. List of elements analyzed.

Table 2. Standard preparation for all elements except Ca, Mg, K, Na.

Table 3. Standard preparation for Ca, Mg, K, Na.

Table 4. ICS Components and Concentration.

Table 5. Recommended analytical isotopes and additional masses to be monitored.

Table 6. Quality Control Items, Frequency, and Corrective Action.

Table 1. List of elements analyzed.

Element	Symbol	CAS#	Reporting Limits		Method	Method
			mg/L	mg/Kg	6020	200.8
Aluminum	(Al)	7429-90-5	0.05	0.5	Aluminum	Aluminum
Antimony	(Sb)	7440-36-0	0.002	0.3	Antimony	Antimony
Arsenic	(As)	7440-38-2	0.001	0.1	Arsenic	Arsenic
Barium	(Ba)	7440-39-3	0.01	1.0	Barium	Barium
Beryllium	(Be)	7440-39-3	0.001	0.50	Beryllium	Beryllium
Boron	(B)	7440-42-8	0.01	1.0	-	-
Cadmium	(Cd)	7440-43-9	0.0005	0.2	Cadmium	Cadmium
Calcium	(Ca)	7440-70-2	0.05	10.0	Calcium	-
Chromium	(Cr)	7440-47-3	1.0	2.0	Chromium	Chromium
Cobalt	(Co)	7440-48-4	0.005	2.0	Cobalt	Cobalt
Copper	(Cu)	7440-50-8	0.01	0.5	Copper	Copper
Iron	(Fe)	7439-89-6	0.004	1.0	Iron	-
Lead	(Pb)	7439-92-1	0.1	1.0	Lead	Lead
Lithium	(Li)	7439-93-2	0.003	1.0	-	-
Magnesium	(Mg)	7439-95-4	0.01	1.0	Magnesium	-
Manganese	(Mn)	7439-96-5	1.0	4.0	Manganese	Manganese
Molybdenum	(Mo)	7439-98-7	0.02	1.0	-	Molybdenum
Nickel	(Ni)	7440-02-0	0.005	0.50	Nickel	Nickel
Potassium	(K)	7440-09-7	0.005	1.0	Potassium	-
Selenium	(Se)	7782-49-2	1.0	5.0	Selenium	Selenium
Silver	(Ag)	7440-22-4	0.005	0.2	Silver	Silver
Sodium	(Na)	7440-23-5	0.0002	0.1	Sodium	-
Strontium	(Sr)	7440-24-6	0.05	10.0	-	-
Tin	(Sn)	7440-31-5	0.005	0.50	-	-
Titanium	(Ti)	7440-32-6	0.02	1.0	-	-
Thallium	(Tl)	7440-28-0	0.005	1.0	Thallium	Thallium
Vanadium	(V)	7440-62-2	0.001	0.50	Vanadium	Vanadium
Zinc	(Zn)	7440-66-6	0.004	1.0	Zinc	Zinc

Table 2. Standard preparation for all elements except Ca, Mg, K, Na.**STANDARD PREPARATION***Inorganic Stock Solution IV-7 + IV-19 (100 ppm)***I. Working Stock Solution 1 (WS1)**

10 mls IV-7 + 10 mls IV-19 + 2 mls HNO₃; Bring to a final volume of 100 mls = 10 ppm

II. Working Stock Solution 2 (WS2)

1ml of WS1 to a final volume of 100 mls = 0.100 ppm

III. Standards

Standards	Volume Working Stock Solution	Internal Standard 5.0 ppm	HNO ₃	1.1. Final Volume
0.20 ppm	2.00 mls WS1	2 mls	2 mls	100 mls
0.10 ppm	1.00 ml WS1	2 mls	2 mls	100 mls
0.05 ppm	0.50 ml WS1	2 mls	2 mls	100 mls
0.02 ppm	20.0 mls WS2	2 mls	2 mls	100 mls
0.01 ppm	10.0 mls WS2	2 mls	2 mls	100 mls
0.005 ppm	5.00 mls WS2	2 mls	2 mls	100 mls
0.002 ppm	2.00 mls WS2	2 mls	2 mls	100 mls
0.0005 ppm	0.50 mls WS2	2 mls	2 mls	100 mls

Table 3. Standard preparation for Ca, Mg, K, Na.

Standards Ppm	Volume of Working Stock	Source and Lot # of Working Stock (100ppm)	Internal Standard 5.0 ppm	HNO ₃	Final Volume
0.50	0.5	High Purity - 620719	2 mls	2 mls	100 mls
1.0	1.0	High Purity - 620719	2 mls	2 mls	100 mls
2.0	2.0	High Purity - 620719	2 mls	2 mls	100 mls
5.0	5.0	High Purity - 620719	2 mls	2 mls	100 mls
10.0	10.0	High Purity - 620719	2 mls	2 mls	100 mls
ICV- 5.0	5.0	Spex – 5-59JB	2 mls	2 mls	100 mls

Table 4. ICS Components and Concentration.

Solution Component	ICS-A (ppm)	ICS-AB (ppm)
Al	100.0	100.0
Ca	100.0	100.0
Fe	100.0	100.0
Mg	100.0	100.0
Na	100.0	100.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.020
Cd	0.0	0.020
Cr	0.0	0.020
Co	0.0	0.020
Cu	0.0	0.020
Mn	0.0	0.020
Ni	0.0	0.020
Ag	0.0	0.020
Zn	0.0	0.020

Table 5a. Recommended analytical isotopes (underlined> and additional masses to be monitored.

Mass	Element	I.S. Used	Elemental Correction	Potential interferences
<u>19</u>	K	Sc, Rh		
<u>22</u>	Ne	Sc, Rh		

24	Mg	Sc, Rh		
43	Ca	Sc, Rh		
44	Ca	Sc, Rh	$(-0.0271)^{(88C)}$	Sr ⁺⁺

- Notes:**
- † Recommended for PE instrument.
 - ‡ Recommended for HP instrument.
 - C = Counts at specified mass.
 - When the concentration of Na in the samples is high, the ionization of Sc is suppressed leading to positive bias of the results, therefore Rh should be used as the internal standard, even if more than 50 amu removed from the element of interest.

Table 5b. Recommended analytical isotopes (underlined> and additional masses to be monitored.

Mass	Element	I.S. Used	Elemental Correction	Potential interferences
6	Li	I.S.	-(0.0813)(⁷ C)	
<u>7</u>	Li	⁶ Li, Sc		
<u>9</u>	Be	⁶ Li, Sc		
10	B	⁶ Li, Sc		
<u>11</u>	B	⁶ Li, Sc		
<u>27</u>	Al	⁶ Li, Sc		
45	Sc	I.S.		CO ₂ H ⁺
47	Ti	⁶ Li, Sc		
<u>49</u>	Ti	⁶ Li, Sc		
<u>51</u>	V	⁶ Li, Sc	-(3.127)(⁵³ C)+(0.352)(⁵² C)	³⁵ ClO ⁺ , ³⁴ SOH ⁺
<u>52</u> [†]	Cr	Sc, Y, Rh		ArC ⁺ , ArO ⁺ , ³⁵ ClHO ⁺
<u>53</u> [‡]	Cr	Sc, Y, Rh		³⁷ ClHO ⁺
<u>54</u> [†]	Fe	Sc, Y, Rh	-(0.0284)(⁵² C)	
<u>55</u>	Mn	Sc, Y, Rh		ArNH ⁺
56	Fe	Sc, Y, Rh		
<u>57</u> [†]	Fe	Sc, Y, Rh		
<u>58</u> [†]	Ni	Sc, Y, Rh		
<u>59</u>	Co	Sc, Y, Rh		
<u>60</u>	Ni	Sc, Y, Rh		
62	Ni	Sc, Y, Rh		TiO
<u>63</u> [†]	Cu	Sc, Y, Rh		³¹ PO ₂ ⁺ , ⁴⁰ ArNa ⁺ , TiO
<u>65</u> [†]	Cu	Sc, Y, Rh		TiO
<u>66</u>	Zn	Sc, Y, Rh		TiO
68	Zn	Sc, Y, Rh		
<u>75</u>	As	Y, Rh	-(3.132)(⁷⁷ C)+(2.736)(⁸³ C)	⁴⁰ Ar ³⁵ Cl ⁺
76	⁴⁰ Ar ³⁶ Ar ⁺	Y, Rh		⁴⁰ Ar ³⁷ Cl ⁺
77	Se	Y, Rh		
<u>78</u> [†]	Se	Y, Rh	-(0.1869)(⁷⁶ C) [‡]	⁴⁰ Ar ³⁸ Ar ⁺
<u>82</u> [†]	Se	Y, Rh		⁸¹ BrH ⁺
83	Kr	Y, Rh		
<u>88</u>	Sr	Y, Rh		
89	Y	I.S.		
90	Zr	Y, Rh		
<u>95</u>	Mo	Y, Rh		⁷⁹ BrO ⁺
98	Mo	Y, Rh	-(0.146)(⁹⁹ C)	⁷⁹ BrHO ⁺
99	Ru	Y, Rh		
103	Rh	I.S.		
105	Pd	Rh		
106	Pd, Cd	Rh		ZrO,
<u>107</u>	Ag	Rh		ZrO
108	MoO	Rh		ZrO, MoO
109	Ag	Rh		ZrO, MoO
<u>111</u>	Cd	Rh		ZrO, MoO
112	Cd	Rh	-(0.040)(¹¹⁸ C)	ZrO, MoO
<u>114</u>	Cd	Rh	-(0.0269)(¹¹⁸ C)	MoO
<u>118</u>	Sn	Rh		
119	Sn	Rh		
120	Sn	Rh	-(0.0127)(¹²⁵ C)	
<u>121</u>	Sb	Rh	-(0.124)(¹²⁵ C)	⁴⁰ Ar ⁸¹ Br ⁺
123	Sb	Rh		
125	Te	Rh		
<u>137</u>	Ba	Rh		
138	Ba	Rh	-(8.91E-04)(¹³⁹ C)-(2.82E-04)(¹⁴⁰ C)	
139	La	Rh		
140	Ce	Rh		
185	Re	I.S.		
203	Tl	Re		
<u>205</u>	Tl	Re		
206	Pb	Re		
207	Pb	Re		
<u>208</u>	Pb	Re	+(1.0)(²⁰⁶ C)+(1.0)(²⁰⁷ C)	

Notes: • † Recommended for the PE instrument.
• ‡ Recommended for the HP instrument.

Table 6. Quality Control Items, Frequency, and Corrective Action.

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tuning	After warm-up. Every 12 hours.	Manufacturer specifications	Check operating parameters, clean cones, replace malfunctioning components if necessary. Reevaluate the tuning.
ICV	After initial calibration.	90-110%	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, and recalibrate the instrument.
ICB	Following ICV.	<RL for water samples	Prepare fresh calibration blank and/or increase the rinse time between analyses; reanalyze ICB; if within limits, continue the run; if still outside limits, determine the source of the problem, make the necessary corrections, and start from the beginning with a new calibration.
BS	After initial calibration.	70-130%	Verify that method parameters are valid, check calibration tables, replace calibration standards if necessary, prepare a fresh calibration blank, and recalibrate the instrument.
CCV	Before and after each batch. Every 10 sample. After re-calibration.	90-110%	Recalibrate the instrument. Follow method specific requirements (6020 or 200.8) as to what data prior to the CCV can be used.
CCB	Following CCV.	<RL for water samples	Prepare fresh calibration blank; reanalyze CCB; if within limits, continue the run; if still outside limits, eliminate the source of the contamination, clean the sample introduction system if necessary, and recalibrate the instrument. Reanalyze all samples from the last good CCB.
LCS	Every batch of 20 samples.	85-115%	Re-digest the entire sample batch and reanalyze.
LRB	Every batch of 20 samples.	<RL for water samples	Re-digest the entire sample batch and reanalyze.
Dp	Every 10 samples.	0-20%	If all other QC acceptable continue the run; sample result should be flagged; otherwise recalibrate instrument and reanalyze samples.
MS	Every 10 samples, prior to digestion.	70-130% with 200.8 75-125% with 6020	For 200.8 flag data if all other QC met; otherwise recalibrate instrument and reanalyze affected samples. For 6020 dilute original sample, re-spike this dilution, and reanalyze until within limits.
MSD [†]	Every 10 samples, prior to digestion.	0-20%	Same as for duplicate.
Dil [‡]	Every batch of 20 samples.	0-10%	If concentration analyzed >100 x MDL, flag data for possible matrix interference.
ICS-A [‡]	Every 12 hours.	<RL for water samples	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument.
ICS-AB [‡]	Every 12 hours.	70-135%	Reevaluate the equations used for corrections, make the necessary adjustments, and recalibrate the instrument.
IS	With every analysis.	60-125% with 200.8 30-120% samples with 6020 80-120% for CCB with 6020	For samples, dilute 4+1 and reanalyze until in control. For CCV/CCB's recalibrate the instrument and reanalyze the affected samples.

NOTE:

- RL = Reporting Limit.
- Dil = Dilution Test.
- † MSD optional instead of duplicate sample.
- ‡ When Method 6020 referenced in the analytical report.

ICP/MS STANDARDS PREP LOG

[illegible]

Exp. Date: _____

Prepared by: Merit Laboratories, Inc.

Source ID	Lot#	Expiration Date
S = Spex		
H = High Purity		
E = ERA		

SOP.082008.REV10.NOV07.DOC

PREP BATCH MTD

2.1. Samples: Water = 0.05 ppm = 50 mls / 0.25 mls of 10 ppm WS1

Soil = 0.10 ppm = 50 mls / 0.50 mls of 10 ppm WS1
WS 1 - Lot # Y-MEB194014 + Z-CICP18146

2) Spike values for minerals (Ca-Mg-K-Na)

LCS = 1.0 ppm = 50 mls / 0.50 mls HP Stock Solution

Samples (Water or Soil) = 2.0 ppm = 50 mls / 1.0 mls HP Stock Solution

High Purity Stock Solution - Lot # 620719

3) HNO₃ Lot # 068109

MICROWAVE ASSISTED ACID DIGESTION OF SOLID SAMPLES

Location:
SOP Files
Metals Laboratory

1.0 SCOPE AND APPLICATION

- 1.1 This digestion procedure is used for the preparation of soils and solid samples for analysis, by inductively coupled plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. The method referenced within this SOP is the EPA SW-846 Method 3050B. This SOP is for use on all samples that do not require Ohio VAP certification.
- 1.2 This method is not a total digestion technique for most samples. The method is a very strong acid digestion that will dissolve almost all elements that could become environmentally available. By design, elements bound in silicate structures are not normally dissolved by this procedure, as they are not usually mobile in the environment.
- 1.3 Samples prepared by using nitric acid digestion are analyzed by ICP-MS for the following metals:

<u>Metal (Symbol)</u>	<u>CAS#:</u>
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Boron (B)	7440-42-8
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-95-4
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Strontium (Sr)	7440-24-6
Thallium (Th)	7440-28-0
Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

2.0 SUMMARY OF METHOD

- 2.1 For the digestion of samples, a representative 0.05-2.0 gram (wet weight) sample is digested with nitric acid (HNO₃) using microwave heating. The resultant digestate is diluted to a final volume of 50 ml. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle prior to analysis.
- 2.2 If required, a separate sample aliquot is reserved for the determination of percent total solids.

3.0 INTERFERENCES

- 3.1 Addition of nitric acid to samples that contain organics could result in a violent reaction and splattering (loss) of the sample, leading to loss of analytes and/or sample, which must be avoided. Sludge samples can contain diverse matrix types, each of which can present its own analytical challenge. Spiked samples and any relevant standard reference material must be processed in accordance with the quality control requirements given in Sec. 8.0.

4.0 APPARATUS AND MATERIALS

4.1 Microwave Digestion System CEM–Model MDS-81D and MARSX Model # 907600

- 4.1.1 The MDS-81D consists of a microwave drying system with an operator selectable power output of 0-600 watts in 1% increments, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon[®] coated cavity, exhaust tubing and standard screen rotating turntable, rotated at 6 rpm to ensure uniform microwave heating
- 4.1.2 The MARSX consists of a microwave drying system with an operator selectable power output of 0 – 1200 watts, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, Teflon[®] coated cavity, exhaust tubing and standard rotating turntable, and self calibration features.
- 4.1.3 Microwave Digestion System Specifications:

MDS-81D		MARSX	
Power	600 Watts	Power	1200 Watts
Pressure	0 - 200 psi	Pressure	0 - 200 psi
Temperature	0 - 200°C	Temperature	0 - 200°C
Capacity	26 samples	Capacity	50 samples

- 4.2 Glass Fiber Filter paper, 0.45 µm.
- 4.3 Membrane Filter paper, 0.45 µm.
- 4.4 Analytical balances, 510 g capacity, minimum accuracy ± 0.001 g, and 250g capacity, minimum accuracy ± 0.0001 g.
- 4.5 Filter funnel, glass, or disposable polypropylene.
- 4.6 Digital bottle top dispenser capable of dispensing volumes of 0-5 ml in 0.02 ml increments.
- 4.7 Disposable Polypropylene vessels, 50 ml, compatible with centrifuge.
- 4.8 Plastic containers to support minimum of 200 ml.
- 4.9 Disposable tongue depressors for sample handling.
- 4.10 Disposable Pasteur pipettes.
- 4.11 Eppendorf automatic pipette with disposable combitips ranging from 2.50 ml to 50 ml capable of pipetting volumes ranging from 50 µl to 5,000 µl.
- 4.12 Centrifuge (IEC Centra GP8)

5.0 REAGENTS

- 5.1 Trace metal grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, if applicable.
- 5.2 Deionized (DI) Water (Type I) is used which meets the specifications of the ASTM standard criteria.
- 5.3 Concentrated nitric acid, HNO₃, Trace Metal Grade. Acid purity is monitored by analysis of the laboratory reagent blank (LRB).

5.4 Standards added to digestion:

5.4.1 Spiking Solutions:

- 5.4.1.1 Multi-element standard solution WS, containing 10 µg/ml each of Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mo, Mn, Ni, Se, Ag, Tl, Ti, V, and Zn. From this solution, 0.50 ml is added to the QC samples (*i.e.* MS/MSD samples), and 0.25 ml to the laboratory control sample (LCS), using the Eppendorf automatic pipette.
- 5.4.1.2 Multi-element standard solution HM (see Appendix 1), containing 100 µg/ml each of Ca, K, Mg, and Na. From this solution, 1.0 ml is added to the QC samples (*i.e.* MS/MSD samples), and 0.50 ml to the laboratory control sample (LCS), using the Eppendorf automatic pipette or by weighing the amounts (1.0 g or 0.50 g) on the scale.

5.4.2 Internal Standards (after digestion):

- 5.4.2.1 Lithium 6, 1000 µg/ml stock solution.
- 5.4.2.2 Scandium, 1000 µg/ml stock solution.
- 5.4.2.3 Yttrium, 1000 µg/ml stock solution.
- 5.4.2.4 Rhodium, 1000 µg/ml stock solution.
- 5.4.2.5 Rhenium, 1000 µg/ml stock solution.

NOTE: *The manufacturer provides the stock solutions with a certificate of analyses and MSDS sheets.*

- 5.4.2.6 Internal Standard working solution (IS-WS): From the above stock solution, 2.5 g of each is transferred to a 1000 ml plastic bottle, along with 10 ml of concentrated HNO₃ and brought to a final volume of 1000 ml (by weight). The concentration in the flask will be 2.5 µg/ml. This represents the internal standards working solution from which 1 ml will be added to all samples (*i.e.* samples, QC samples, blanks, etc.) prior to the analysis by the ICP/MS.

5.4.3 Spiking Solutions:

- 5.4.3.1 Spiking solutions are prepared according to the Standard Prep Log. The formula, date source solutions, lot numbers, expiration date of stock standards, expiration date standard made, expiration and unique ID of any working standards used.
- 5.4.3.2 All standards are NIST traceable.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 6.1 Soil samples are collected without preservation, usually in glass containers with Teflon lined caps. Non-aqueous samples must be refrigerated at 4±2 degrees Celsius.
- 6.2 Holding times for metals are 6 months from the date of sampling, with the exception of Mercury which is not covered in this SOP.

7.0 PROCEDURE^[1]

- 7.1 Calibration of Microwave Equipment.
 - 7.1.1 Microwaves are calibrated once a year according to the manufacturer's instructions
- 7.2 All digestion vessels are disposable and are used only once. This allows for better sample control and prevents cross contamination.

^[1] "Microwave digestion for metals", EPA SW 846 Method 3050B, Update III, 1998 for calibration of the microwave and Method 3051 for the digestion of solid samples.

7.3 Sample Digestion^[2]

CAUTION: *-Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system.
- Loss of sample through splattering inside the microwave system needs to be avoided. Physical observation is sufficient to determine if this is the case, therefore the batch of samples needs to be inspected at the end of the digestion cycle. If splattering has occurred, the samples are to be discarded, and a new batch is to be prepared.*

- 7.3.1 Mix the sample thoroughly to achieve homogeneity. Transfer 0.2 to 0.3 grams sample (wet weight) for a soil matrix or 0.05 to 2 grams sample (wet weight) for liquidy sludges and other various solid matrices to a digestion vessel, and record the weight on the preparation sheet, to a minimum of 0.001 g. Ten milliliters DI water is used for LCS and LRB.
- 7.3.2 Add 1 ml of concentrated HNO₃ to each sample vessel, mixing the slurry, then wait 5-10 minutes for any reaction to occur.
- 7.3.3 After the acid has had some time to react add 10ml DI water.
- 7.3.4 With every batch of samples, pipette 1 ml of concentrated HNO₃ into a vessel labeled Laboratory Reagent Blank (LRB), which is carried through the entire digestion procedure, similar to an analytical sample. For every 20, samples pipette 1 ml of concentrated HNO₃ into a vessel labeled Laboratory Control Sample (LCS), which is carried through the entire digestion procedure, similar to an analytical sample. For every 20 samples measured, as described at 7.3.1 and 7.3.2, a sample is designated for analysis as a Matrix Spike (MS) and Matrix Spike Duplicate (MSD) or Duplicate (Dp).
- 7.3.5 For all metals, except Ca, Mg, K, and Na, add 0.50 ml of the QC spiking solution to the LCS, and 1.0 ml to the MS/MSD samples. For Ca, Mg, K and Na, add 1.0 ml of the **HM** solution to the LCS, and 1.0 ml to the MS/MSD samples. The spike concentration and the Lot # of the stock solution used is recorded in the digestion log. The spike solution for MS/MSD is added before digestion. For samples prepared for use with method 6020 or 6020A a post-digestion spike is employed if the regular spike fails to meet the QC criteria.
- 7.3.6 Samples are slowly ramped in the microwave to 95±4 degrees Celsius over the course of a few minutes and maintained at this temperature for 5 minutes without boiling.
- 7.3.7 Allow samples to set for 5 minutes then repeat step 7.3.6.
- 7.3.8 After the temperature program is completed, leave the vessels 5-10 minutes in the microwave, to cool down, and then move them into the hood. Add 1 ml of the Internal Standard working solution using an Eppendorf automatic pipettor and dilute to the 50 ml mark with DI Water, into a calibrated (per lot) digestion vessel.
- 7.3.9 A post-digestion spike is performed as necessary and prepared as follows: take a 25 ml aliquot of the sample designated for MS/MSD and add to it 0.50 ml of the QC spiking solution (for all elements except Ca, Mg, K, and Na). For Ca, Mg, K, and Na add 1.0 ml of the **HM** solution.
- 7.3.10 If the digested sample contains particulate matter, which may clog the nebulizer, the sample may be centrifuged, allowed to settle over night, or filtered.
- 7.3.10.1 Centrifugation: Centrifugation at 4500 rpm for 3 minutes is usually sufficient to clear the supernatant.

7.3.10.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.10.3 Filtering: The filtering apparatus (flask and funnel) must be thoroughly rinsed with a 10% v/v nitric acid solution and copious amounts of DI Water. Filter the sample through a 0.45 µm filter paper and transfer the liquid to a new vessel. Glass fiber filters are acceptable for all metals except Zn and Ba, for which membrane filters are required, due to the presence of these elements in the glass fiber filters.

7.3.11 Calculate the dilution factor (DF) by the formula:

$$DF = \frac{\text{Final Volume (50)}}{\text{Sample amount}} \times \frac{100}{\% \text{ Total solids}}$$

7.3.12 This is recorded in the sample preparation log and is used in the determination of the final result by the ICP/MS.

8.0 QUALITY CONTROL

- 8.1 For each analytical batch of 20 samples processed, one laboratory reagent blank (LRB) must be carried throughout the entire sample preparation and analytical process. The LRB will be used in determining if the samples are being contaminated during preparation or from reagents.
- 8.2 For each analytical batch of 20 samples processed, one laboratory control sample (LCS) must be carried throughout the entire sample preparation and analytical process. The LCS will be used in determining the performance of the method for that particular batch.
- 8.3 Spiked samples (MS) must be employed to determine accuracy. A spiked sample must be included with each batch of 20 samples processed.
- 8.4 Duplicate (Dp) samples or Matrix Spike Duplicate (MSD) must be processed for every 20 samples or less.

9.0 WASTE DISPOSAL

9.1 Samples

- 9.1.1 All digested samples are neutralized with baking soda and diluted before being disposed of with the normal laboratory waste water.
- 9.1.2 As a "small generator" of metals, Merit Laboratories has been approved for this type of disposal from the local government.

9.2 Acid bottles

- 9.2.1 Acid bottles are rinsed out and neutralized with baking soda before being disposed of with the normal laboratory waste.

10.0 DOCUMENTATION

9.1 Metals digestion log sheet must contain the following information:

- Date.
- Analyst initials.
- Method reference.
- Sample #.
- Sample weight or volume.
- MS/MSD/LCS spike concentration.
- Total solids (if applicable)

- Acid Lot #
- Spike Lot #
- Dilution Factor
- Prep batch
- Final volume of sample

11.0 METHOD PERFORMANCE

- 11.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

12.0 REFERENCES

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- 12.6 Hinnners, T.A., Heithmar, E., Rissmann, E., and Smith, D., Winter Conference on Plasma Spectrochemistry, Abstract THP18; p. 237, San Diego, CA (1994).
- 12.7 Lichte, F.E., et al., Anal. Chem. 59, 1150 (1987).
- 12.8 Evans E.H., and Ebdon, L., J. Anal. At. Spectrom. 4, 299 (1989).
- 12.9 Beauchemin, D., et al., Spectrochim. Acta 42B, 467 (1987).
- 12.10 Houk, R.S., Anal. Chem. 58, 97A (1986).
- 12.11 Thompson, J.J., and Houk, R.S., Appl. Spectrosc. 41, 801 (1987).
- 12.12 SW-846, Method 6020 Revision 0, 1994.
- 12.13 Method 200.8, Revision 5.4, 1998.
- 12.14 SW-846, Method 6020A Revision 1, 2007
- 12.15 SW-846, Method 8000C Revision 3, 2003
- 12.16 SW-846, Method 3050B Revision 2, 1996
- 12.17 1985 Annual Book of ASTM Standards, Vol.11.01; "Standard Specification for Reagent Water"
- 12.18

13.0 SAFETY

- 13.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 13.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 4 times per hour and 6 times per hour when the emergency purge button is hit.
- 13.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.
- 13.4 Specific attention be paid (but not limited) to
- 13.4.1 Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.
 - 13.4.2 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.
 - 13.4.3 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

14.0 APPROVAL & ISSUE:

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

_____ Analyst	_____ Date
_____ Andy Ball, QA Officer	_____ Date
_____ Maya V. Murshak, Technical Director	_____ Date

1.0 SCOPE AND APPLICATION

- 1.1 This SOP is for cold-vapor atomic absorption (CVAA) procedure is used for determining the concentration of mercury in drinking water. Drinking water mercury is run by EPA Method 245.1.

2.0 SUMMARY OF METHOD

- 2.1 Prior to analysis, the samples are prepared according to the procedure discussed in this SOP.
- 2.2 The cold-vapor atomic absorption technique is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height or peak area) is measured as a function of mercury concentration.
- 2.3 Typical detection limit for this method is 0.2 µg/L. This range may be extended above or below the normal range by increasing or decreasing sample size or by optimizing instrument sensitivity. With the operating conditions and parameters stated in this SOP, a detection limit as low as 0.008 µg/L, with a practical quantitation limit of 0.05 µg/L can be obtained without difficulty.

3.0 INTERFERENCES

- 3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.
- 3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.
- 3.3 Seawaters, brines, and industrial effluents high in chlorides require additional potassium permanganate (as much as 7.5 ml) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.
- 3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. The indication that an organic interference is present is usually suggested by peak broadening, with increase in the retention approximately 0.4-0.5 minutes more than the retention time of the calibration standards.
- 3.5 For qualitative purposes, ICP/MS verification is possible to confirm the presence of mercury.

4.0 APPARATUS AND MATERIALS

- 4.1 Automated Mercury Analyzer, (Quick Trace Mercury analyzer M-7500 consisting of the following components:
- 4.1.1 Computer-controlled 4-channel high-performance peristaltic pump (12-roller pump head).
- 4.1.2 Computerized thermally ozone-free Hg lamp with a thermally controlled Hg lamp housing (for a stabilized Hg vapor lamp).
- 4.1.3 Stable high performance Gas-Liquid Separator (GLS). Non-foaming/non-bubbling "thin liquid film" GLS design, which allows trouble-free direct analysis of blood, urine, and fish tissue digests as well as standard water and waste analysis.
- 4.1.4 Integrated ASX-510 Auto Sampler for accommodation of calibration standards and up to 360 samples.
- 4.2 Block Digester
- 4.3 Polypropylene digestion vessels.
- 4.4 VWR Brand Digital Pipettor dispensing variable volumes from 100 to 1000 µl.
- 4.5 Pipette Dispenser Bottles with adjustable volume 0 - 5 ml in 0.2 ml increments.
- 4.6 Graduated cylinder 100 ml, 1000 ml or equivalent.
- 4.7 Disposable Pasteur pipettes.
- 4.8 Disposable Serological pipettes, 0-10 ml in 0.1 ml increments, 0-5 ml in 0.1 ml increments, and 0-1 ml in 0.01 ml increments.
- 4.9 Disposable plastic cups.
- 4.10 Analytical balance, 310 g capacity, minimum accuracy ± 0.001 g.

5.0 REAGENTS

- 5.1 Reagent water (Deionized water): All references to reagent water in the method refer to ASTM Type I water (ASTM D1193), unless otherwise specified.
- 5.2 Sulfuric acid (H_2SO_4), concentrated: Trace metal grade. Shelf Life 3 years, follow lot expiration date
- 5.3 Nitric acid (HNO_3), concentrated: Trace metal grade. Shelf Life 3 years, follow lot expiration date
- 5.4 Stannous chloride: 35 ml HCl brought to 500 ml of 10% H_2SO_4 then add 50 g stannous chloride (SnCl_2).
- 5.5 Hydroxylamine hydrochloride solution ($\text{NH}_2\text{OH}\cdot\text{HCl}$): Dissolve 120 g of sodium chloride and 120 g of Hydroxylamine hydrochloride in 1000 g reagent water.
- 5.6 Potassium permanganate (KMnO_4), 5% solution (w/v): Dissolve 50 g of potassium permanganate in 1000 g of reagent water.
- 5.7 Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), 5% solution (w/v): Dissolve 50 g of potassium persulfate in 1000 ml of reagent water.
- 5.8 Stock mercury solutions: 10 ppm mercury solutions from SPEX CertiPrep (**SPEX**) and High Purity Standards (**HPS**). Working standards made by taking 1 mL of stock standard and bringing to 100 mL with DI Water.
- 5.9 The HPS stock solution is used for preparing calibration standards; the SPEX stock solution is used for preparing the initial calibration verification (ICV) standard.
 - 5.9.1 Mercury working standard: Dilute the stock mercury solution to obtain a working standard containing 100 $\mu\text{g/L}$ mercury (1 g of the stock solution to 100 g reagent water, on the scale). The working solutions should be prepared fresh before making standards. Acidity of the working standard should be maintained at 7% HCl (v/v). This acid (7 ml) should be added immediately after measuring the standard aliquot, and before dilution to final volume (100 g). [According to instrument documentation calibration standards contain 7% HCl.]

Note: All reagents purchased for Mercury analyses are of high purity (ACS Reagent Grade or better). Verification is done by the laboratory through the analysis of the reagent blank (LRB).

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 6.1 All samples are collected in appropriate containers. For water samples, the samples are collected in HNO_3 pre-preserved plastic container, ensuring acidification to pH of < 2.
- 6.2 Holding times for Mercury is 28 days.

7.0 PROCEDURE

- 7.1 Sample Preparation:
 - 7.1.1 In a polypropylene vessel add 25 ml sample (25 g on the scale for aqueous samples), The amount of sample used is recorded in the digestion log.
 - 7.1.2 Repeat this procedure for a batch of 20 samples.
 - 7.1.3 With each batch, include a matrix duplicate and a matrix spike for every 10 samples. A Laboratory Control Sample (LCS), and a Laboratory Reagent Blank (LRB) for every 20 samples.
 - 7.1.4 Add 1.25 ml concentrated H_2SO_4 , 0.62 ml concentrated HNO_3 , and 3.75 ml KMnO_4 , to all vessels, and 0.5 ml of the 100 ppb HPS working standard solution to the QC samples (i.e. LCS, MS/MSD, etc.).
 - 7.1.5 Wait 15 minutes. Check if KMnO_4 is still in solution. If the purple color is gone, add more KMnO_4 (Section 3.3), record the amount added, and make corrections to the dilution factor for that particular sample (see Section 7.1.10). If the solution is still purple, proceed to step 7.1.3.
 - 7.1.6 Add 2 ml $\text{K}_2\text{S}_2\text{O}_8$ to each vessel.

- 7.1.7 Turn on block digester and place vessels in it. Bring the temperature at about $95 \pm 3^\circ$ and heat for 2 hours.
- 7.1.8 Let the vessels cool and add 1.5 ml of Hydroxylamine hydrochloride solution.
- 7.1.9 Calculate the dilution factor (*DF*) by the formula:

$$DF = \frac{\text{Final Volume (25)}}{\text{Sample amount}} \times CF$$

If needed, calculate the correction factor (*CF*) due to additional KMnO_4 (*x*):

$$CF = \frac{35.14 + x}{35.14}$$

This is recorded in the sample digestion log, and is used in the determination of the mercury result by the CVAA analyzer.

7.2 Calibration Procedure:

- 7.2.1 Prepare 7 point calibration curve: From the HPS working standard solution weigh out aliquots of 0.0 ml, 0.1 ml, 0.2 ml, 0.5 ml, 1.0 ml, 2.0 ml, 6.0 ml and 10 ml in 8 Teflon bottles (125 ml) then add 5 ml H_2SO_4 , 2.5 ml HNO_3 , 15 ml KMnO_4 , 8 ml $\text{K}_2\text{S}_2\text{O}_8$, 6 ml Hydroxylamine Hydrochloride, 7 ml HCl , and bring to 100 ml. This will provide a calibration curve of 0.0, 0.1, 0.2, 0.5, 1.0, 2.0, 6.0, 10.0 $\mu\text{g/L}$. The minimum acceptable correlation coefficient is 0.997.
- 7.2.2 Prepare in a similar manner an Initial Calibration Verification (ICV) standard made from a different source (SPEX Certiprep) at a concentration of 5.0 $\mu\text{g/L}$, to verify the calibration. In addition, for verifying the calibration solution, an optional ERA standard can be used. The ERA standard comes with performance acceptance limits established by ERA, and is prepared according to the instructions, by taking 1 ml(g) of the concentrate, dilution to 100 ml(g) with reagent water, followed by the steps described in section 7.2.1.
- 7.2.3 Continuing Calibration Verification (CCV) standard is also prepared as in 7.2.1 from the HPS working standard, to a concentration of 2.0 $\mu\text{g/L}$.
- 7.2.4 The standard solutions described above must be kept in sealed Teflon bottles, and are to be prepared every 2 weeks, although they are stable for at much longer when kept as above. Usually, the CCV standard is prepared more often because it is used more frequent than the other solutions. The LCS is used to evaluate the performance of the method and is to be prepared with every batch, from fresh mercury working standard.

7.3 Sample Analysis:

- 7.3.1 Turn on the Mercury Analyzer and allow it to warm up for one hour to be able to analysis ppb's and three hours to be able to analysis ppt's.
- 7.3.2 Transfer the appropriate standards and samples to the labeled vials, and load the auto-sampler starting with the calibration standards, calibration verification samples, and the batch of samples to be analyzed (QC samples included).
- 7.3.3 Start the Quick Trace program.
 - 7.3.3.1 Click on the instrument button then the analyzer button
 - 7.3.3.2 Set the pump to 50% and the gas to 100 ml/minute
- 7.3.4 Check to make sure the reagent has a smooth segmented flow. Once this has be established se the pump speed to 100% and the gas flow to 300 ml/minute.
 - 7.3.4.1 Disconnect the GLS exhaust tubing and crimp the waste tubing just before the mixing tee.
 - 7.3.4.2 This will wet the GLS center post after this is done reset the pump speed to 50% and the gas flow to 100 ml/minute.
 - 7.3.4.3 Wait for the water to drain out of the GLS and then attach the GLS exhaust tubing.
- 7.3.5 Place the reagent capillary in the reagent bottle and appropriate tubing in to the rinse solution.
- 7.3.6 Type in the number of samples that you are running. The go into method editor and click read sample to zero mercury analyzer and pick a standard.
- 7.3.7 Verify the baseline and peak are correct for the standard.
- 7.3.8 Exit method editor and press start to analyze samples

7.4 Data Reporting: The instrument reports final mercury concentrations as $\mu\text{g/L}$ for aqueous samples.

8.0 QUALITY CONTROL

- 8.1 All quality control data must be maintained and available for easy reference or inspection.
- 8.2 Initial Demonstration of Performance.
- 8.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic range) and laboratory performance (determination of method detection limit) prior to analyses conducted by this method.
- 8.2.2 Linear calibration ranges - The upper limit of the linear calibration range must be established for mercury by determining the signal responses from a minimum of three different concentration standards. Linear calibration ranges must be determined every year or whenever a significant change in instrument response is observed.
- 8.3 A mercury MDL (Method Detection Limit) is established using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit. To determine MDL values, take seven replicate aliquot of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$
 where: t = Student's t value for a 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom is, $t = 3.14$ for seven replicates.
 S = standard deviation of the replicate analyses. A MDL is determined every year or whenever a significant change in background or instrument response is expected (e.g., detector change)
- 8.4 Assessing Laboratory Performance
- 8.4.1 The lab must analyze at least one LRB (Laboratory Reagent Blank) with each set of 20 or less samples. LRB data is used to assess contamination from the lab environment and to characterize spectral background from the reagents used in sample processing. If a mercury value in a LRB exceeds the MDL, then lab or reagent contamination is suspect. Any determined source of contamination must be eliminated and the samples redigested and reanalyzed.
- 8.4.2 The lab must analyze at least one Laboratory Fortified Blank (LFB), also known as Laboratory Control Sample (LCS), with each batch of 20 samples or less. Calculate accuracy as percent recovery. If recovery of mercury falls outside control limits, the method is judged out of control. The source of the problem must be identified and resolved before continuing analyses. Control limits for the LFB are 85-115%.
- 8.5 Assessing Analyte Recovery - Laboratory Fortified Sample Matrix
- 8.5.1 The lab must add a known amount of mercury to a minimum of one in ten samples or one sample per sample set, whichever is greater. Select a water sample that is representative of the type of water sample being analyzed.
- 8.5.2 Calculate the percent recovery, corrected for background concentrations measured in the unfortified sample. Control limits for fortified sample matrix is 80% to 120%. Percent recovery is calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{S} \times 100$$

where R = percent recovery

C_s = fortified sample concentration

C = sample background concentration

S = concentration equivalent of fortifier added to water sample

8.5.3 If mercury recovery falls outside the designated range, and the lab performance is shown to be in control, the recovery problem encountered with the fortified water sample is judged to be matrix related, not system related. The result for mercury in the unfortified sample must be flagged to inform the data user that the results are suspect due to matrix effects.

8.6 Calibration curves must be composed of a minimum of a blank and seven standards.

8.7 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

- 8.8 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.
- 8.9 Verify calibration with an independently prepared check standard every 10 samples. This is accomplished by the use of the CCV.
- 8.10 Run one spike and duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.
- 8.11 For Drinking water samples an additional CCV is run at the start of the run to check the calibration with a solution from the same source as the calibration. This CCV run has an acceptance criteria of $\pm 5\%$.
- 8.12 The method allows for the use of the method of standard addition (MSA) to be used on samples with complex matrix that results in odd viscosity or surface tension. Merit has yet to find this useful for drinking water samples. Therefore, this information has been omitted from this SOP. For more information on this, please see SOP #087470 or SOP #082008.
- 8.13 Summary of the QC requirements and performance acceptance limits are shown in the following table:

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and re-digest samples.	Notify client. Flag data.
Initial Calibration Blank (ICB)	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and re-digest samples.	Notify client. Flag data.
Continuing Calibration Blank (CCB)	Yes Following calibration	<MDL or 1/10 Regulatory limit	Rerun last 10 samples.	Notify client. Flag data.
Laboratory Control Sample (LCS) also known as Laboratory Fortified Blank (LFB)	Yes 1/20 samples	85%-115%	Re-digest the sample set.	Notify client. Flag data.
Continuing Calibration Verification (CCV)	Yes 1/10 samples	90%-110%	All samples bracketed by a CCV outside the acceptable control limits must be re-digested and re-analyzed.	Notify client. Flag data.
Matrix Duplicate or Matrix Spike Duplicate	Yes 1/10 samples	RPD<20%	Re-digest samples and QC.	Notify client. Flag data.
Matrix Spike	Yes 1/ 10 samples	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Initial Calibration Verification (ICV)	At the start of every analytical run	90%-110%	Re-calibration and re-run ICV	Notify client. Flag data.
Dilution & Rerun	No except if result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	Notify client. Flag data.
Additional Continuing Calibration Verification (CCV)	At the start of every analytical run	95% - 105%	Re-calibration and re-run CCV	

9.0 DOCUMENTATION

- 9.1 Mercury Digestion Log
 - 9.1.1 Start Time
 - 9.1.2 Stop Time
 - 9.1.3 Temperature
 - 9.1.4 Prep Batch ID
 - 9.1.5 Date
 - 9.1.6 Analyst
 - 9.1.7 Sample #
 - 9.1.8 Bottle ID
 - 9.1.9 Sample Amount
 - 9.1.10 Dilution Factor
 - 9.1.11 Final Volume
 - 9.1.12 Spike Values
 - 9.1.13 Standards Lot #'s

10.0 METHOD PERFORMANCE

- 10.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes. The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

11.0 REFERENCES

- 11.1 EPA METHOD 245.1

12.0 SAFETY

- 12.1 Eye protection and gloves must be worn while performing mercury analyses.
- 12.2 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 12.3 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
- 12.4 A reference file of material safety data sheets (MSDSs) is available to all personnel.
- 12.5 Specific attention be paid (but not limited) to
 - 12.5.1 Concentrated sulfuric acid is toxic and damaging to skin and mucus membranes. If eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents.
 - 12.5.2 Hydrochloric acid is corrosive, extreme heat or contact with metals can release flammable hydrogen gas, stable under ordinary conditions of use and storage, and incompatible with many substances and highly reactive with strong bases, metals, metal oxides, hydroxides, amines, carbonates, cyanides, sulfides, sulfites, and formaldehyde.
 - 12.5.3 Nitric acid is a corrosive, not combustible, but substance is a strong oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition, and can react with metals to release flammable hydrogen gas.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

- 13.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.
- 13.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.0 APPROVAL & ISSUE:

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

Analyst	Date
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Andy Ball, QA Officer	Date
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Maya V. Murshak, Technical Director	Date
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MERCURY IN WATERS, SOLIDS, AND WASTES (COLD-VAPOR TECHNIQUE)**1.0 SCOPE AND APPLICATION**

- 1.1 Cold-vapor atomic absorption (CVAA) procedure is used for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters, soils, solid and sludge-type wastes.

2.0 SUMMARY OF METHOD

- 2.1 Prior to analysis, the samples are prepared according to the procedure discussed in this SOP.
- 2.2 The cold-vapor atomic absorption technique is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height or peak area) is measured as a function of mercury concentration. Method references include SW846 7470A and 7471A, and 245.1.
- 2.3 Typical detection limit for this method is 0.2 µg/L. This range may be extended above or below the normal range by increasing or decreasing sample size or by optimizing instrument sensitivity. With the operating conditions and parameters stated in this SOP, a detection limit as low as 0.005 µg/L, with a practical quantitation limit of 0.05 µg/L can be obtained without difficulty. Solid reporting limits range from 0.005 mg/kg to 0.10 mg/kg.

3.0 INTERFERENCES

- 3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.
- 3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.
- 3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 7.5 ml) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.
- 3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. The indication that an organic interference is present is usually suggested by peak broadening with increase in the retention approximately 0.4-0.5 min more than the retention time of the calibration standards.
- 3.5 For qualitative purposes, ICP/MS verification is possible to confirm the presence of mercury.

4.0 APPARATUS AND MATERIALS

- 4.1 Quick Trace Mercury Analyzer M-7500 consisting of the following components:
- 4.1.1 Computer-controlled 4-channel high-performance peristaltic pump (12-roller pump head).
- 4.1.2 Computerized thermally ozone-free Hg lamp with a thermally controlled Hg lamp housing (for a stabilized Hg vapor lamp).
- 4.1.3 Stable high performance Gas-Liquid Separator (GLS). Non-foaming/non-bubbling "thin liquid film" GLS design, which allows trouble-free direct analysis of blood, urine, and fish tissue digests as well as standard water and waste analysis.

- 4.1.4 Integrated ASX-510 Auto Sampler for accommodation of calibration standards and up to 360 samples.
 - 4.2 Digestion block
 - 4.3 Polypropylene digestion vessels.
 - 4.4 VWR Brand Digital Pipettor dispensing variable volumes from 100 to 1000 µl.
 - 4.5 Pipette Dispenser Bottles with adjustable volume 0 - 5 ml in 0.2 ml increments.
 - 4.6 Graduated cylinder 100 ml, 1000 ml or equivalent.
 - 4.7 Disposable Pasteur pipettes.
 - 4.8 Disposable Serological pipettes, 0-10 ml in 0.1 ml increments, 0-5 ml in 0.1 ml increments, and 0-1 ml in 0.01 ml increments.
 - 4.9 Disposable plastic cups.
 - 4.10 Analytical balance, 300 g capacity, minimum accuracy ± 0.01 g.
 - 4.11 Filter funnel, glass or disposable polypropylene.
 - 4.12 Glass-fiber filter paper, 0.45 µm.
- 5.0 REAGENTS
- 5.1 Reagent water (Deionized water): All references to reagent water in the method refer to ASTM Type I water (ASTM D1193), unless otherwise specified.
 - 5.2 Sulfuric acid (H_2SO_4), concentrated: Trace metal grade, indefinite shelf live.
 - 5.3 Sulfuric acid, 10% (v/v): Measure 900 g reagent water on the scale and add to it 100 ml of concentrated sulfuric acid in the hood. Prepare as needed, indefinite shelf live.
 - 5.4 Nitric acid (HNO_3), concentrated: Trace metal grade, indefinite shelf live.
 - 5.5 Stannous chloride: Add 25 g stannous chloride (SnCl_2) and 25 g sodium chloride (NaCl) to 500 ml of 10% H_2SO_4 . Prepare as needed, can be stored for 30 days.
 - 5.6 Hydroxylamine hydrochloride solution ($\text{NH}_2\text{OH}\cdot\text{HCl}$): Dissolve 120 g of sodium chloride and 120 g of Hydroxylamine hydrochloride in 1000 g reagent water. Prepare as needed, indefinite shelf live.
 - 5.7 Potassium permanganate (KMnO_4), 5% solution (w/v): Dissolve 50 g of potassium permanganate in 1000 g of reagent water. Prepare as needed, indefinite shelf live.
 - 5.8 Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), 5% solution (w/v): Dissolve 50 g of potassium persulfate in 1000 ml of reagent water. Prepare as needed, indefinite shelf live.
 - 5.9 Stock mercury solutions: 10 ppm mercury solutions from SPEX CertiPrep (**SPEX**) and High Purity Standards (**HPS**).
 - 5.10 Mercury working standard: Dilute of the stock mercury solution to obtain a working standard containing 100 µg/L mercury (1 g of the stock solution to 100 g reagent water, on the scale). The HPS stock solution is used for preparing calibration standards; the SPEX stock solution is used for preparing the initial calibration verification (ICV) standard. The working solutions should be prepared fresh before making standards or preparing samples. Acidity of the working standard should be maintained at 1% HCl (v/v). This acid (1 ml) should be added immediately after measuring the standard aliquot, and before dilution to final volume (100 g).

Note: All reagents purchased for Mercury analyses are of high purity (ACS Reagent Grade or better). Verification is done by the laboratory through the analysis of the reagent blank (LRB).

Note: The stock solutions are NIST traceable, and provided with a certificate of analyses and MSDS sheets by the vendor.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 6.1 All samples are collected in appropriate containers. For water samples, the samples are collected in HNO₃ pre-preserved plastic container, ensuring acidification to pH of < 2. Soil samples are collected without preservation, usually in glass containers with Teflon lined caps.
- 6.2 Holding times for Mercury is 28 days. Refrigerate soil samples @ 4°C.

7.0 PROCEDURE

7.1 Sample Preparation:

7.1.1 Liquids

- 7.1.1.1 In a polypropylene vessel measure (with a disposable serological pipette) 25 ml/g sample or a smaller amount, if the sample is expected to foam or if it is not aqueous, and dilute to 25 ml (g) with reagent water. The amount of sample used is recorded in the preparation log.
- 7.1.1.2 Repeat this procedure for a batch of 20 samples. If the batch does not have 20 samples, fill the rest of the tubes with reagent water.
- 7.1.1.3 With each batch include a matrix duplicate and a matrix spike for every 10 samples, a Laboratory Control Sample (LCS), and a Laboratory Reagent Blank (LRB).
- 7.1.1.4 Add 1.25 ml concentrated H₂SO₄, 0.66 ml concentrated HNO₃, and 3.75 ml KMnO₄, to all vessels, and 0.5 ml of the 100 ppb HPS working standard solution to the QC samples (i.e. MS/MSD, etc.). The LCS is prepared the exact same way, but instead of sample, uses DI water plus 0.05 ml of the HPS working standard.

7.1.2 Solids:

- 7.1.2.1 In a polypropylene tube weigh out approximately 0.5 g sample, and dilute to 25 ml (g) with reagent water.
- 7.1.2.2 The amount of sample used is recorded in the preparation log. Repeat this procedure for a batch of 20 samples. If the batch does not have 20 samples, fill the rest of the tubes with reagent water.
- 7.1.2.3 With each batch include a matrix duplicate and a matrix spike for every 10 samples, a Laboratory Control Sample (LCS), and a Laboratory Reagent Blank (LRB). Add 1.25 ml concentrated H₂SO₄, 0.66 ml concentrated HNO₃, and 3.75 ml KMnO₄, to all vessels, and 0.5 ml of the 100 ppb HPS working standard solution to the QC samples (i.e. LCS, MS/MSD, etc.). The LCS is prepared the exact same way, but instead of sample, uses DI water plus 0.05 ml of the HPS working standard.

- 7.1.3 Wait 15 min. Check if KMnO₄ is still in solution. If the purple color is gone, add more KMnO₄ (Section 3.3), record the amount added, and make corrections to the dilution factor for that particular sample (see Section 7.1.10 for correction to the dilution factor). If the solution is still purple, proceed to step 7.1.3.

- 7.1.4 Add 2 ml K₂S₂O₈.

- 7.1.5 Place the vessels in block digester

- 7.1.5.1 heat water samples at 95°C for 2 hours
 - 7.1.5.2 heat soil samples at 95°C for 30 minutes.

- 7.1.6 Let the vessels cool and add 1.5 ml of Hydroxylamine hydrochloride solution.

- 7.1.7 If the digested sample contains particulate matter, which may clog some of the valves of the mercury analyzer, the sample may be centrifuged or filtered.

7.1.8 Centrifugation: Centrifugation at 4500 rpm for 5 minutes is usually sufficient to clear the supernatant.

7.1.9 Filtering: The filtering apparatus (flask and funnel) must be thoroughly washed with warm water and soap, and rinsed with a 10% v/v nitric acid solution and copious amounts of DI Water. Filter the sample through a 1.0 µm filter paper and transfer the liquid to a new vessel.

7.1.10 Calculate the dilution factor (DF) by the formula:

$$DF = \frac{\text{Final Volume (25)}}{\text{Sample amount}} \times \frac{100}{\% \text{ Total solids}} \times CF$$

If needed, calculate the correction factor (CF) due to additional KMnO_4 (x):

$$CF = \frac{35.16 + x}{35.16}$$

This is recorded in the sample preparation log, and is used in the determination of the mercury result by the CVAA analyzer.

7.2 Calibration Procedure:

7.2.1 Prepare 5 point calibration curve: From the HPS working standard solution weigh out aliquots of 0.0 ml, 0.1 ml, 0.2 ml, 0.5 ml, 1.0ml, 2.0 ml, 4.0ml, and 10.0 ml to 8 Teflon bottles (125 ml) and dilute to 100 ml (g). Follow the steps described in the sample preparation above, adding 4x of each reagent, and without heating. This will provide a calibration curve of 0.0, 0.1, 0.2, 0.5, 1.0, 2.0, 4.0, 10.0 µg/L. The minimum acceptable correlation coefficient is 0.997.

7.2.2 Prepare in a similar manner an Initial Calibration Verification (ICV) standard made from a different source (from the SPEX stock solution) at a concentration of 5.0 µg/L, to verify the calibration. In addition, for verifying the calibration solution, an optional ERA standard can be used. The ERA standard comes with performance acceptance limits established by ERA, and is prepared according to the instructions provided by ERA, by taking 1 ml (g) of the concentrate, dilution to 100 ml (g) with reagent water, followed by the steps described in section 7.2.1.

7.2.3 Continuing Calibration Verification (CCV) standard is also prepared as in 7.2.1 from the HPS working standard, to a concentration of 2.0 µg/L. An optional Upper Limit standard of 30 µg/L can be included with the analytical run.

7.2.4 The standard solutions described above must be kept in sealed Teflon bottles, and are to be prepared every 4 weeks, although they are stable for at much longer when kept as above. Usually, the CCV standard is prepared more often because it is used more frequent than the other solutions. The LCS is used to evaluate the performance of the method and is to be prepared with every batch, form fresh mercury working standard.

7.3 Sample Analysis:

7.3.1 Turn on the Mercury Analyzer and allow it to warm up for one hour to be able to analysis ppb's and three hours to be able to analysis ppt's.

7.3.2 Transfer the appropriate standards and samples to the labeled vials, and load the auto-sampler starting with the calibration standards, calibration verification samples, and the batch of samples to be analyzed (QC samples included).

7.3.3 Once the analyzer is warmed up turn on the gas flow to the instrument.

- 7.3.4 Start the Quick Trace program.
 - 7.3.4.1 Click on the instrument button then the analyzer button
 - 7.3.4.2 Set the pump to 50% and the gas to 100 ml/minute
 - 7.3.5 Check to make sure the reagent has a smooth segmented flow. Once this has been established set the pump speed to 100% and the gas flow to 300 ml/minute.
 - 7.3.5.1 Disconnect the GLS exhaust tubing and crimp the waste tubing just before the mixing tee.
 - 7.3.5.2 This will wet the GLS center post after this is done reset the pump speed to 50% and the gas flow to 100 ml/minute.
 - 7.3.5.3 Wait for the water to drain out of the GLS and then attach the GLS exhaust tubing.
 - 7.3.6 Place the reagent capillary in the reagent bottle and appropriate tubing in to the rinse solution.
 - 7.3.7 Type in the number of samples that you are running. Then go into method editor and click read sample to zero mercury analyzer and pick a standard
 - 7.3.8 Verify the baseline and peak are correct for the standard.
 - 7.3.9 Exit method editor and press start to analyze samples
 - 7.4 Data Reporting: The instrument reports final mercury concentrations as µg/L for aqueous samples, and mg/Kg dry weight (where appropriate) for solid samples.
- 8.0 QUALITY CONTROL
- 8.1 All quality control data should be maintained and available for easy reference or inspection.
 - 8.2 Initial Demonstration of Performance.
 - 8.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic range) and laboratory performance (determination of method detection limit) prior to analyses conducted by this method.
 - 8.2.2 Linear calibration ranges - The upper limit of the linear calibration range should be established for mercury by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Linear calibration ranges should be determined initially, and whenever a significant change in instrument response is observed.
 - 8.2.3 A mercury MDL (Method Detection Limit) is established using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:
$$MDL = (t) \times (S)$$
where t is student's t value for a 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom ($t = 3.14$ for seven replicates), and S is the standard deviation of the replicate analyses. A MDL is determined annually or whenever a significant change in background or instrument response is expected (e.g. detector change).
 - 8.3 Assessing Laboratory Performance.

- 8.3.1 The laboratory must analyze at least one LRB with each batch of 20 samples of samples. LRB data is used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing. If a mercury value in a LRB exceeds 2.2 x MDL or the reporting limit for liquid samples, whichever is greater, laboratory or reagent contamination is suspected. Any determined source of contamination should be eliminated and the batch re-digested and re-analyzed.
- 8.3.2 The laboratory must analyze at least one LCS with each batch of 20 samples. Calculate accuracy as percent recovery. If recovery of mercury falls outside control limits (85-115%), the method is judged out of control. The source of the problem should be identified and resolved and new aliquots of the samples redigested and reanalyzed.
- 8.3.3 Instrument performance:
- 8.3.3.1 The calibration curve correlation coefficient should be ≥ 0.997 . If this is not achieved prepared fresh standards and re-analyze.
 - 8.3.3.2 Check instrument calibration by analyzing the initial calibration verification solution (ICV), made from a source different than the calibration standards (Section 5.10), and the initial calibration blank (ICB). Corrective action listed in Section 8.3.3.4.
 - 8.3.3.3 Verify calibration at a frequency of every 10 analytical samples with the CCV standard and the continuing calibration blank (CCB). These solutions must also be analyzed at the beginning of the analysis and after the last sample.
 - 8.3.3.4 The results of the ICV and CCV must agree within $\pm 10\%$ of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Reanalyze the samples if the last CCV was outside $\pm 15\%$ of expected value.
 - 8.3.3.5 The results of the ICB and CCB's must be less than 2.2 times the current MDL or less than the reporting limits for liquid samples, whichever is greater. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed.

8.4 Assessing Analyte Recovery and Data Quality.

- 8.4.1 The laboratory must analyze matrix spike (MS) with every 10 samples. Calculate the percent recovery of each analyte, corrected for background concentrations measured in the unfortified (original) sample. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{S} \times 100$$

where: R = percent recovery.

C_s = spiked sample concentration.

C = sample background concentration.

S = concentration equivalent of analyte added to fortify the sample.

The recovery limits for MS samples are 70-130%. If the recovery falls outside the designated range, and the laboratory performance is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the recovery problem encountered with the spiked sample is judged to be matrix related, not system related. The data user should be informed that the result for the unspiked sample is suspect due to matrix interference. Recovery is not required if the concentration of the mercury added is less than 30% of the concentration of mercury in the original sample.

8.4.2 Analyze one matrix duplicate (Dp) sample for every 10 samples. In some cases, a matrix spike duplicate (MSD) can be used instead of the matrix duplicate, especially if the analyte in the sample is of low concentration. A control limit of 20% RPD should not be exceeded for measured mercury concentration greater than 100 times the MDL. If this limit is exceeded and laboratory performance for that analyte is shown to be in control (ICV/ICB, CCV/CCB, and LCS/LRB within the limits), the problem encountered is judged to be matrix related. The data user should be informed that the result for that analyte is suspect due to the heterogeneous nature of the sample. If the performance of the laboratory is not in control (ICV/ICB, CCV/CCB, and LCS/LRB outside the limits), the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition for that analyte must be reanalyzed.

8.4.3 Summary of Quality Control Criteria:

QC Item	Frequency	QC Limits
ICV	Following calibration.	90-110%
ICB	Following calibration	<RL liquid samples.
CCV	Before and after each batch. Every 10 samples.	90-110%
CCB	Before and after each batch. Every 10 samples.	<RL liquid samples.
LCS	Every batch of 20 samples.	85-115%
LRB	Every batch of 20 samples.	<RL liquid samples.
Dp	Every 10 samples.	0-20%
MS	Every 10 samples.	70-130%
MSD	Every 10 samples.	0-20%

Note: RL = Reporting Limit.

9.0 METHOD PERFORMANCE

- 9.1 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.
- 9.2 Performance Evaluation samples are analyzed periodically in order to prove the performance of the method.

10.0 APPROVAL & ISSUE:

Analyst Date

Andy Ball, QA Officer Date

Maya V. Murshak, Technical Director Date

**SOP #033000: ION CHROMATOGRAPHY FOR ANALYZING
ANIONS (CHLORIDE, FLUORIDE, NITRATE, NITRITE, BROMIDE & SULFATE)
USING THE DX-100 DIONEX ION CHROMATOGRAPH**

Revision: 6
Date: 5/12/10

Location: QA Officer's Office
Wet Chemistry Laboratory

1.0 SCOPE

- 0.1 This method is applicable to drinking, surface, ground waters, treated mixed wastewater and some industrial process waters, such as boilerwater and cooling water as long as samples are filtered through a 0.5 micron filter. (Metrigard, Glass Fiber Filter, 47mm /GE Water & Process Technologies)

2.0 SUMMARY OF THE METHOD

- 2.1 This SOP is a procedure for evaluating Anions, (Chloride, Sulfate, Nitrate-N, Nitrite-N, Fluoride & Bromide) in liquid samples.
- 2.2 A water sample is injected into a stream of carbonate-bicarbonate eluent and passed through a series of ion exchangers. The anions of interest are separated on the basis of their relative affinity for a low capacity, strongly basic anion exchanger (guard & separator columns). The separated anions are directed onto a strongly acidic cation exchanger (suppressor). The anions are then converted to their highly conductive acid forms and the eluent is converted to weakly conductive carbonic acid. The separated anions are then measured by conductivity. They are identified on the basis of retention time as compared to standards. Quantitation is by measurement of peak area or peak height.

3.0 INTERFERENCES

- 3.1 Any substance that has a retention time coinciding with that of any anions to be determined will cause interferences. Some low-molecular-weight organic acids interfere with chloride and fluoride. High concentration of any one ion also interferes with the resolution of others. Sample dilution overcomes many interferences. To resolve uncertainties of identification use the method of known addition.

4.0 REAGENTS

- 4.1 Deionized (DI) water
- 4.2 Stock Eluent, sodium bicarbonate – sodium carbonate: Dissolve 1.908g Na₂CO₃ and 1.428g NaHCO₃ in water and dilute to 100ml. Prepared every 2 months or when stock eluent bottle starts running low.
- 4.3 Working eluent: Pipet 10ml of stock eluent to a 1 L volumetric flask and dilute to volume. Made up fresh when eluent bottle runs low.
- 4.4 Control ERA
- 4.5 Standard Anion solutions:
- 4.5.1 Chloride (Hach Std) 1,000ppm. Cat # 183-49. Expiration listed on standard bottle.
 - 4.5.2 Sulfate (Hach Std) 1,000ppm Cat # 21757-49. Expiration listed on standard bottle.
 - 4.5.3 Fluoride (Hach Std) 100ppm Cat # 232-49. Expiration listed on standard bottle.
 - 4.5.4 Nitrate-N (Hach Std) 100ppm Cat # 1947-49. Expiration listed on standard bottle.
 - 4.5.5 Bromide (KBr) (Hach) 1,000ppm Cat # 11270-34 Dissolve: 0.1489g KBr in water and dilute to 100ml, *See stock solutions prep log*, Prepared fresh every 3 months. KBr shelf life is 5 years.
 - 4.5.6 Nitrite-N (NaNO₂) (Hach) 100ppm Cat # 2452-01 Dissolve: 0.0498g NaNO₂ in water and dilute to 100ml, *See stock solutions prep log*. Prepared fresh every 48 hours as need. NaNO₂ shelf life is 5 years.

5.0 APPARATUS & MATERIALS

- 5.1 Ion Chromatograph (DX-100 Dionex)
- 5.2 Anion separator column, resolves Br⁻; Cl⁻; SO₄²⁻; NO₃⁻; NO₂⁻; F⁻ and PO₄³⁻ (not run with this method)
- 5.3 Guard column, protects separator column.
- 5.4 Self-Regenerating suppressor, converts eluent and separated anions to their acid forms.

**SOP #033000: ION CHROMATOGRAPHY FOR ANALYZING
ANIONS (CHLORIDE, FLUORIDE, NITRATE, NITRITE, BROMIDE & SULFATE)
USING THE DX-100 DIONEX ION CHROMATOGRAPH**

Revision: 6
Date: 5/12/10

- 5.5 5ml polyvials with filtercaps
- 5.6 50ml centrifuge tubes with screw caps
- 5.7 Filtering apparatus & 0.5 micron filters (Metrigard, Glass Fiber Filter, 47mm /GE Water & Process Technologies)
- 5.8 Auto-pipettors (.05 – 1mL)

6.0 SAMPLE HANDLING AND PRESERVATION

- 6.1 Samples should be collected in unpreserved high-density polyethylene containers. All bottles purchased by Merit are pre-cleaned certified.
- 6.2 Analyze samples needing Nitrite and/or Nitrate as soon as possible, not exceeding 48 hours. Maximum holding time for water samples from the time of sampling is 28 days for Chloride, Sulfate, Fluoride, & Bromide. Sample must be refrigerated at 4±2 degrees C.

7.0 PROCEDURE

7.1 System Startup and Test

- 7.1.1 Turn the system power on and set the *Control* button on the system Panel to Relay. Make sure computer, printer and autosampler are also on.
- 7.1.2 Confirm system air is working and pressure is between 50 and 60 psi.
- 7.1.3 Confirm that the eluent container is at least half full before a run. If not, make up working eluent: Add new working eluent by the following
 - 7.1.3.1 Turn eluent pressure switch to off (should be set at 5psi).
 - 7.1.3.2 Take cap off eluent container and slowly add working eluent, replace cap and swirl to mix.
 - 7.1.3.3 Re-pressurize eluent container by turning eluent switch to on.
 - 7.1.3.4 Open valve below Pulse Damper and allow to bleed for 1 minute.
- 7.1.4 Ensure pump flow rate adjustment is correct (180 = 1.8ml/min).
- 7.1.5 Make sure detector range is set to operating range 30 uS.
- 7.1.6 Check waste container, if close to full empty before startup.
- 7.1.7 Open Run program. Click on Load / Method / norm.met. Instrument will begin startup. After approximately 20 seconds, open up valve below pulse damper again to rid any air and to reprime pump. Close valve again before system pressure drops to zero (around 8 seconds).
- 7.1.8 Let system equilibrate for at least 45 minutes before running samples (Conductivity reading should be between 15 and 17).
- 7.1.9 Set Low Limit pressure switch to on.

7.2 Running the Analysis

- 7.2.1 All samples must be filtered through 0.5 micron filters prior to being analyzed.
- 7.2.2 All Anion runs begin with a Blank, Blank Spike, ERA Control and LCS.
- 7.2.3 Fill polyvial with 5ml of sample to be tested.
- 7.2.4 Place filtercap on polyvial and push to top of vial with filtercap tool.
- 7.2.5 The sample can now be placed in autosampler tray.
- 7.2.6 Open schedule program; Double-click to setup IC run.
- 7.2.7 Type in sample ID under **Sample Name**; Norm.met under **Method**; the date of run under **Data File**, ex.(090501); & dilution factor under **Dil**.
- 7.2.8 Click on **File; Save As** (type in date); click **ok**.
- 7.2.9 Go to Run program, click on **Load; Schedule**, scroll through to find schedule just set and click **ok**.
- 7.2.10 Push **Run** button on autosampler the 1st tray will then load.
- 7.2.11 Push green **Run** button on Computer Interface. The scheduled run will now begin.

7.3 Calibration

- 7.3.1 Inject calibration standards containing a mixture of all anions and determine approximate retention times. Approximate times: Fluoride (0.97min), Chloride

**SOP #033000: ION CHROMATOGRAPHY FOR ANALYZING
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- (1.53min), Nitrite-N (1.85min), Bromide (2.87min), Nitrate-N (3.30min), and Sulfate (6.80min). This is always the order of retention.
- 7.3.2 Next, prepare 5 different calibration standards for each anion all in one mixture, (See Section 5.4).
- 7.3.3 Run these 5 calibration standards with a blank proceeding the run, following the procedure in 7.2.2 through 7.2.10
- 7.3.4 A calibration coefficient of 0.999 or greater is necessary for working calibration curve. If less than 0.999, then rerun.
- 7.3.5 A calibration curve can now be plotted in the **Cal Plot / Norm.Meth** program. Open the Cal Plot program by double clicking on icon, click on **File**, double-click on **norm.meth**, click on **Edit**, click on **component table**.
- 7.3.6 From the component table each anions calibration curve can now be plotted by entering the peak height and area against the concentration.
- 7.3.7 Recalibration must be done when changing columns, changing any detector settings, when retention times begin to shift, when QC samples begin to fall outside the methods limits, or every 6 months.

8.0 CALCULATIONS

7.1 Equation $C = H \times F \times D$

where:

C = mg anion / L

H = peak area,

F = response factor = concentration of standard / area of standard,
and

D = dilution factor for those samples requiring dilution.

Note: This calculation is automatically performed by software when sample is run, so the result on chromatograph for each anion is final result as long as dilution factor was entered before run.

9.0 QUALITY CONTROL

9.1 See Table 1

9.2 A sample batch will consist of 20 samples unless noted below. The QC samples that are analyzed per batch are:

- Method Blank
- Blank Spike
- Control (ERA or another outside known)
- LCS (every 10 samples for drinking water matrix)
- Matrix Spike (every 10 samples for drinking water matrix)
- Matrix Spike Dup (every 10 samples for Level 3)
- Matrix Duplicate (every 10 samples for drinking water matrix)

**SOP #033000: ION CHROMATOGRAPHY FOR ANALYZING
ANIONS (CHLORIDE, FLUORIDE, NITRATE, NITRITE, BROMIDE & SULFATE)
USING THE DX-100 DIONEX ION CHROMATOGRAPH**

Revision: 6
Date: 5/12/10

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Laboratory Control Sample (LCS) Soluble or insoluble	Yes Every 10 drinking Water / One every sample set	90%-110%	Rerun	Notify client. Flag data.
Matrix Duplicate	Yes Every 10 drinking Water / One every sample set	RPD<15%	Rerun entire set	Notify client. Flag data.
Matrix Spike	Yes Every 10 drinking Water / One every sample set	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Matrix Spike Duplicate	Level 3 One every 10 samples			Notify client. Flag data.
Dilution & Rerun	No except if result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	Notify client. Flag data.

10.0 DOCUMENTATION

- 10.1 Ion Chromatograph raw data
- 10.2 Ion Chromatograph schedule log

11.0 METHOD PERFORMANCE

- 11.1 Precision and accuracy studies are performed on as needed basis.
- 11.2 Method Detection Limit studies are performed every 6 months.

12.0 SAFETY

- 12.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 12.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
- 12.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

- 13.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.
- 13.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.0 REFERENCES

- 14.1 Method 300.0, Revision 2.2, 1999

**SOP #033000: ION CHROMATOGRAPHY FOR ANALYZING
ANIONS (CHLORIDE, FLUORIDE, NITRATE, NITRITE, BROMIDE & SULFATE)
USING THE DX-100 DIONEX ION CHROMATOGRAPH**

Revision: 6
Date: 5/12/10

15.0 APPROVAL & ISSUE:

15.1 The following personnel have read, accepted and approved this standard operating practice.

Analyst	Date
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Andy Ball, QA Officer	Date
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Maya Murshak, Technical Director	Date
----------------------------------	------

Location: SOP Files
QA Officer's Office
Wet Chemistry Laboratory

1.0 SCOPE

- 1.1 This SOP is applicable to drinking, surface, and saline water, domestic and industrial wastes.
- 1.2 The SOP is suitable for all concentration ranges of hardness; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 25-mg CaCO_3 .

2.0 SUMMARY OF THE METHOD

- 2.1 This SOP is a procedure for evaluating Total Hardness as CaCO_3 in liquid samples.
- 2.2 Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction, using indicator, has a red color in the presence of Ca and Mg and a blue color when they're sequestered.

3.0 INTERFERENCES

- 3.1 When in excessive amounts, some heavy metal ions interfere by causing fading or indistinct end points.

4.0 APPARATUS AND MATERIALS

- 4.1 Digital titrator
- 4.2 Stir plate
- 4.3 Clear plastic cups
- 4.4 Stir Bar
- 4.5 Graduated Cylinder
- 4.6 Pipette
- 4.7 Analytical Balance

5.0 REAGENTS

- 5.1 Deionized (DI) water
- 5.2 0.080 EDTA tetrasodium titration cartridge
- 5.3 0.800 EDTA tetrasodium titration cartridge, used for samples of known or suspected high concentration
- 5.4 Hach Buffer Solution Hardness 1
- 5.5 Hach ManVer® 2 Hardness indicator powder pillows
- 5.6 10,000 mg/L calcium, total hardness as CaCO_3 standard
- 5.7 5N Sodium Hydroxide (NaOH)

6.0 SAMPLE HANDLING AND PRESERVATION

- 6.1 Hardness is best analyzed as soon as possible from the time the sample is collected. Holding time for water samples is 180 days refrigerated at $4 \pm 2^\circ\text{C}$
- 6.2 Samples must be provided in unpreserved, clear plastic bottles. When samples are received in Nitric acid preserved bottles, samples must be neutralized with NaOH before analysis.

7.0 PROCEDURE

7.1 Color Development and Measurement

- 7.1.1 Pour 100 mL of DI water in a clear plastic cup to make a Blank sample.
- 7.1.2 Place a magnetic stirring bar in the cup and place the cup on a stir plate. Turn on stir plate so that the sample is stirred well, but its color is still clearly visible.
- 7.1.3 Add 1.0 mL buffer solution to sample.
- 7.1.4 Pour one Hach ManVer® 2 Hardness indicator powder pillow in the cup.
- 7.1.5 Using a digital titrator set up with a 0.080 EDTA tetrasodium titration cartridge, place its tip in the sample so that the acid may be released into the sample. Slowly turn the end piece clockwise until the water just turns from its original pink color to blue.
- 7.1.6 The number of digits used to do this is the value for the Blank. This value will be subtracted from the digit values of all other samples.
- 7.1.7 Rinse off magnetic stir bar.
- 7.1.8 Analyze quality control samples by following Sections 7.1.2 to 7.1.7.

- 7.1.9 Place 10 mL of a sample in another cup and add 90 mL DI water to it. Repeat Sections 7.1.2 to 7.1.7 to find the number of digits needed to titrate the sample. If this value is exceedingly small or large, the dilution of the sample may be adjusted

8.0 CALCULATIONS

$$8.1 \text{ Hardness mg CaCO}_3/\text{L} = \frac{D * 100\text{mL}}{S} \times M$$

Where D = number of Digits used in titration of sample

M = multiplier number specified by concentration of cartridge (in this case, 1.0)

S = mL of sample used

9.0 QUALITY CONTROL

9.1 See Table 1

9.2 Samples are analyzed in batches of twenty or less per QC set. The QC samples that are analyzed per batch are:

- Control
- MS
- LCS
- DUP
- MSD (optional if set is not Level 3)
- Method Blank
- Blank Spike

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation)	Yes	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify Client. Flag Data.
Blank	One each set			
Laboratory Control Sample (LCS)	Yes One each set	90%-110%	Rerun	Notify Client. Flag Data.
Blank Spike	Yes One each set	90%-110%	Rerun	Notify Client. Flag Data.
Control	Yes One each set	90%-110%	Rerun	Notify Client. Flag Data.
Matrix Duplicate	Yes One each set	RPD<20%	Rerun entire set	Notify Client. Flag Data.
Matrix Spike	Yes One each set	80%-120%	Analyze by Method of Standard Additions	Notify Client. Flag Data.
Matrix Spike Duplicate	Level 3 One each set	80%-120%	Analyze by Method of Standard Additions	Notify Client. Flag Data.

10.0 DOCUMENTATION

10.1 Hardness Bench Sheet

- 10.1.1 Analyst
- 10.1.2 Date Run
- 10.1.3 Method #
- 10.1.4 Detection Limit
- 10.1.5 Program #
- 10.1.6 Wavelength

- 10.1.7 Titrant
- 10.1.8 Merit #
- 10.1.9 Dilution
- 10.1.10 Digit Multiplier
- 10.1.11 Digits
- 10.1.12 Total Solids %
- 10.1.13 Final Concentration (mg/L)
- 10.1.14 Spike (mg/L)
- 10.1.15 % Recovery
- 10.1.16 Source/Lot #
- 10.1.17 Run Time

11.0 METHOD PERFORMANCE

- 11.1 Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.)
- 11.2 Method Detection limit studies are performed annually.

12.0 REFERENCES

- 12.1 EPA Water NPDES, Method 130.2, EPA Test Methods, Revision 1982, Hardness, Total (mg/L as CaCO_3 , Titrimetric, EDTA)
- 12.2 Standard Methods, Method 2340, 20th Edition.

13.0 SAFETY

- 13.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 13.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
- 13.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.
- 13.4 Specific attention be paid (but not limited) to
 - 13.4.1 Sodium hydroxide is corrosive, causes burns to any area of contact, can slowly pick up moisture from air and react with carbon dioxide from air to form sodium carbonate, and in contact with acids and organic halogen compounds, especially trichloroethylene, sodium hydroxide may causes violent reactions.

14.0 WASTE DISPOSAL AND POLLUTION PREVENTION

- 14.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.
- 14.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

15.0 APPROVAL & ISSUE:

- 15.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP should acknowledge their comprehension of the SOP with a signature and a date.

Analyst _____ Date _____

Andy Ball, QA Officer _____ Date _____

Maya V. Murshak, Technical Director _____ Date _____

Location: QA Officer's Office
SOP Files
Wet Chemistry Laboratory

1.0 SCOPE

- 1.1 This SOP is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
- 1.2 The SOP is suitable for all concentration ranges; however, appropriate aliquots should be used to avoid a titration volume greater than 50 mL.

2.0 SUMMARY OF THE METHOD

- 2.1 This SOP is a procedure for evaluating Total, Bicarbonate, and Carbonate Alkalinity in liquid samples. Alkalinity is run by Method 2320B.

3.0 INTERFERENCES

- 3.1 Matrix interferences are due to sample color, samples may need to be diluted.

4.0 APPARATUS AND MATERIALS

- 4.1 Digital titrator
- 4.2 Stir plate
- 4.3 Magnetic Stir bar
- 4.4 Clear plastic cups
- 4.5 Pipettors

5.0 REAGENTS

- 5.1 Deionized (DI) water
- 5.2 0.1600 sulfuric acid titration cartridge
- 5.3 Bromcresol Green-Methyl Red indicator pillow packets
- 5.4 Phenolphthalein Indicator Powder Pillow
- 5.5 25,000 mg/L alkalinity standard, 10 mL of standard brought to 100 mL with DI Water

6.0 SAMPLE HANDLING AND PRESERVATION

- 6.1 Alkalinity is best analyzed as soon as possible from the time the sample is collected. Holding time for water samples is 14 days refrigerated at $4^{\circ}\text{C} \pm 2^{\circ}\text{C}$
- 6.2 Samples must be provided in unpreserved, clear plastic bottles.

7.0 PROCEDURE

- 7.1 Samples must be brought to room temperature before analysis.
- 7.2 COLOR DEVELOPMENT AND MEASUREMENT (TOTAL ALKALINITY ONLY)
 - 7.2.1 Pour 100 mL of DI water in a clear plastic cup to make a Blank sample.
 - 7.2.2 Place a magnetic stirring bar in the cup and place the cup on a stir plate. Turn on stir plate so that the sample is stirred well, but its color is still clearly visible.
 - 7.2.3 Pour one Bromcresol Green-Methyl Red indicator powder pillow in the cup.
 - 7.2.4 Using a digital titrator set up with a 0.1600 sulfuric acid titration cartridge, place its tip in the sample so that the acid may be released into the sample. Slowly turn the endpiece clockwise until the water just turns from its original green color to pink/purple.
 - 7.2.5 The number of digits used to do this is the value for the Blank. This value will be subtracted from the digit values of all other samples.
 - 7.2.6 Rinse off magnetic stir bar.
 - 7.2.7 Run all quality control samples (i.e. control, blank spike, LCS) by following Sections 7.2.2 to 7.2.4.
 - 7.2.8 Place 100 mL of a sample in another cup. Repeat Sections 7.2.2 to 7.2.4 to find the number of digits needed to titrate the sample. If this value is exceedingly small or large, the dilution of the sample may be adjusted.

7.3 CARBONATE AND BICARBONATE MEASUREMENT

7.3.1 Place 100 mL of sample in cup, add the contents of a Phenolphthalein Indicator Powder pillow and swirl to mix.

7.3.1.1 If there is no color change, dilute and titrate following Section 7.2.

7.3.1.2 If there is a color change to pink, dilute and titrate to a colorless endpoint. Record the number of digits required as the Phenolphthalein Alkalinity. (Do not reset digit counter!) Continue titration following Section 7.2. Record the number of digits required.

8.0 CALCULATIONS

$$8.1 \text{ Total Alkalinity, } \frac{\text{mg}}{\text{L}} \text{ CaCO}_3 = \frac{D * 100\text{mL} * M}{S}$$

Where: D = number of digits used in titration of sample

M = multiplier number specified by concentration of cartridge (in this case, 0.1)

S = mL of sample used

$$8.2 \text{ Phenolphthalein Alkalinity, } \frac{\text{mg}}{\text{L}} \text{ CaCO}_3 = \frac{D * 100\text{mL} * M}{S}$$

Where: D = number of digits used in titration of sample

M = multiplier number specified by concentration of cartridge (in this case, 0.1)

S = mL of sample used

8.3 See Table 2 Alkalinity Relationship for how to calculate Bicarbonate and Carbonate Alkalinity

9.0 QUALITY CONTROL

9.1 See Table 1

9.2 Samples are analyzed in batches of twenty or less per QC set. The QC samples that are analyzed per batch are:

- Control
- MS
- LCS
- DUP
- MSD (optional/ Level 3)
- Method Blank
- Blank Spike (every 10 samples)

10.0 DOCUMENTATION

10.1 Alkalinity Bench Sheet

- 10.1.1 Analyst
- 10.1.2 Date Run
- 10.1.3 Method #
- 10.1.4 Detection Limit
- 10.1.5 Program #
- 10.1.6 Wavelength
- 10.1.7 Titrant
- 10.1.8 Merit #
- 10.1.9 Dilution
- 10.1.10 Digit Multiplier
- 10.1.11 Digits
- 10.1.12 TS %
- 10.1.13 Final Concentration (mg/L)
- 10.1.14 Spike (mg/L)
- 10.1.15 % Recovery
- 10.1.16 Source/ Lot #
- 10.1.17 Run Time

11.0 METHOD PERFORMANCE

11.1 Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.)

11.2 Method Detection limit studies are performed annually.

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation)	Yes	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Blank	One each set			
Laboratory Control Sample (LCS)	Yes	85%-115%	Rerun	Notify client. Flag data.
Soluble or insoluble	One each set			
Control	Yes	85%-115%	Rerun	Notify client. Flag data.
	One each set			
Blank Spike	Yes	85%-115%	Rerun	Notify client. Flag data.
	One every 10 samples			
Matrix Duplicate	Yes	RPD<20%	Rerun entire set	Notify client. Flag data.
	One each set			
Matrix Spike	Yes	85%-115%	Analyze by Method of Standard Additions	Notify client. Flag data.
	One each set			
Matrix Spike Duplicate	Yes	85%-115%	Analyze by Method of Standard Additions	Notify client. Flag data.
	One every 20 samples Level 3			

Table 2. Alkalinity Relationship

Row	Result of Titration	Carbonate Alkalinity is equal to:	Bicarbonate Alkalinity is equal to:
1	Phenolphthalein Alkalinity = 0	0	Total Alkalinity
2	Phenolphthalein Alkalinity equal to Total Alkalinity	0	0
3	Phenolphthalein Alkalinity less than one half of Total Alkalinity	2 times the Phenolphthalein Alkalinity	Total Alkalinity minus two times Phenolphthalein Alkalinity
4	Phenolphthalein Alkalinity equal to one half of Total Alkalinity	Total Alkalinity	0
5	Phenolphthalein Alkalinity greater than one half of Total Alkalinity	2 time the difference between Total and Phenolphthalein Alkalinity	0

To use the Table 2 follow these steps;

- Does the phenolphthalein alkalinity equal zero? If yes, use Row 1.
- Does the phenolphthalein alkalinity equal total alkalinity? If yes, use Row 2.
- Multiply the phenolphthalein alkalinity by 2.

- d) Select Row 3, 4, or 5 based on comparing the result of Step c with the total alkalinity.
- e) Perform the required calculations in the appropriate row.

12.0 REFERENCES

- 12.1 *Standard Methods*, twentieth edition, Method 2320B, Alkalinity.
- 12.2 Hach Digital Titrator Model 16900-01 Manual. Alkalinity.

13.0 SAFETY

- 13.1 Eye protection and gloves must be worn while performing alkalinity analyses.
- 13.2 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 13.3 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
- 13.4 A reference file of material safety data sheets (MSDSs) is available to all personnel.

14.0 WASTE DISPOSAL AND POLLUTION PREVENTION

- 14.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.
- 14.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

15.0 APPROVAL & ISSUE:

- 15.1 This section indicates which personnel have read, accepted, and approved the SOP. All analysts involved with the SOP should acknowledge their comprehension of the SOP with a signature and a date.

Analyst	Date
---------	------

Andy Ball, QA Officer	Date
-----------------------	------

Maya V. Murshak, Technical Director	Date
-------------------------------------	------

1.0 SCOPE AND APPLICATION

- 1.1 This method is applicable to the measurement of ammonia-nitrogen in drinking, surface and saline waters, domestic and industrial wastes, and soils. Reporting limit for 0.02 mg/l for liquids and 1 mg/kg for soils.
- 1.2 This method covers the range from 0.02 to 15 mg NH₃ -N/L. Color and turbidity has no effect on the measurements, thus, distillation is unnecessary.
Nitrogen CAS # N 7727-37-9
Ammonia, NH₃ CAS # 7664-41-7

2.0 SUMMARY OF METHOD

- 2.1 The ammonia is determined potentiometrically using an ion selective ammonia electrode and a pH meter having an expanded millivolt scale or a specific ion meter. Standard Method 4500 NH₃ D is used.
- 2.2 The ammonia electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an ammonium chloride internal solution. Ammonia in the sample diffuses through the membrane and alters the pH of the internal solution, which is sensed by a pH electrode. The constant level of chloride in the internal solution is sensed by a chloride selective ion electrode which acts as the reference electrode.

3.0 INTERFERENCES

- 3.1 Volatile amines act as a positive interference.
- 3.2 Mercury interferes by forming a strong complex with ammonia. Thus the samples cannot be preserved with mercuric chloride.

4.0 APPARATUS AND MATERIALS

- 4.1 Electrometer (pH meter) with expanded mV scale
- 4.2 Ammonia selective electrode
- 4.3 Magnetic stirrer, thermally insulated, and Teflon-Coated stirring bar.
- 4.4 Plastic cups

5.0 REAGENTS

- 5.1 Deionized water: Special precautions must be taken to ensure that the deionized water is free of ammonia. This is accomplished by passing deionized water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin.
- 5.2 Sodium hydroxide (NaOH), 10N
- 5.3 Environmental Resource Associates quality control nutrients standards
- 5.4 Ammonium chloride, standard: Hach solutions 1000mg/l
- 5.5 Concentrated Sulfuric Acid (H₂SO₄)

6.0 SAMPLE HANDLING AND PRESERVATION

- 6.1 Liquid samples must be collected in 250 mL polyethylene plastic bottle pre-preserved with 2 mL of concentrated H₂SO₄ and stored at 4±2°C. Soil samples are collected in glass jars without preservative and stored at 4±2°C.
- 6.2 The holding time for water and soil ammonia samples is 28 days from sampling.

7.0 PROCEDURE

- 7.1 Samples need to be brought to room temperature before being analyzed.
- 7.2 Probe is rinsed with 100 mL deionized water containing 1 mL of NaOH at the beginning of the procedure and between samples.
- 7.3 Preparation of standards: Hach pre-prepared Standards
- 7.4 Calibration of electrometer: Place 100 mL of each standard solution in clean plastic cups. Immerse electrode into standard of lowest concentration and add 1 mL of 10N sodium hydroxide solution while mixing. Keep electrode in the solution until a stable reading is obtained.

NOTE 1: *The pH of the solution after the addition of NaOH must be above 11. Caution: sodium hydroxide must not be added prior to electrode immersion, for ammonia can be lost from a basic solution.*

- 7.5 Repeat this procedure with the remaining standards, going from lowest to highest concentration. Plot the concentration of ammonia in mg NH₃-N/L on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.
- 7.6 Calibration of a specific ion meter: Follow the directions of the manufacturer for the operation of the instrument.
- 7.7 Sample measurement: Follow the procedure in Section 7.2 for 100 mL of liquid sample or 0.1 g to 5 g of soil with 100 ml of deionized water in plastic cups. Record the stabilized potential of each unknown sample and convert the potential reading to the ammonia concentration using the standard curve.
- 7.8 Calculations:

$$HN3-N/L=(A)(B)$$

Where:

A = dilution factor

B = concentration of NH₃-N mg/l from curve

8.0 QUALITY CONTROL

- 8.1 Quality Control Samples for up to twenty samples per batch include:

- 8.1.1 1 method blank (Deionized water)
- 8.1.2 2 standards (1 ppm and 10 ppm) to establish a curve.
- 8.1.3 Calibration Check (5ppm)
- 8.1.4 Laboratory Control Sample (LCS) (2.5 ppm) at a mid-point concentration
- 8.1.5 Control, ERA, from a different source than the calibration curve
- 8.1.6 Matrix Spike (MS) per 20 samples
- 8.1.7 Matrix Spike Duplicate (MSD) (required Level 3)
- 8.1.8 Sample duplicate (DUP) per 20 samples
- 8.1.9 Extra standards to include concentrations of sample set (0.02ppm, 0.1 ppm, 10 – 15 ppm)

- 8.2 See Table 1 for all quality control items, frequency, limits, and corrective actions.

9.0 METHOD PERFORMANCE

Method detection limit studies are performed annually.

10.0 EQUIPMENT MAINTENANCE AND TROUBLESHOOTING

All equipment shall be maintained and calibrated according to manufacturer's procedures. When equipment is not performing as required, the instrument shall not be used until it is recalibrated or replaced.

11.0 SAFETY

- 11.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 11.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
- 11.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.
- 11.4 Specific attention be paid (but not limited) to
- 11.4.1 Concentrated sulfuric acid is toxic and damaging to skin and mucus membranes. If eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents.
 - 11.4.2 Sodium hydroxide is corrosive, causes burns to any area of contact, can slowly pick up moisture from air and react with carbon dioxide from air to form sodium carbonate, and in contact with acids and organic halogen compounds, especially trichloroethylene, sodium hydroxide may cause violent reactions.

12.0 WASTE DISPOSAL AND POLLUTION PREVENTION

SOP #033503: NITROGEN, AMMONIA (NH₃)
POTENTIOMETRIC, ION SELECTIVE ELECTRODE
STANDARD METHOD 4500 NH₃ D

Revision: 9
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- 12.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.
- 12.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.
- 12.3 Sample waste is made acidic by adding concentrated sulfuric acid, neutralized with baking soda, and then disposed of down the drain.

13.0 DEFINITIONS

- 13.1 Sample Batch: Samples of the same or similar matrix; for this method, a sample batch consists of 20 samples or less.
- 13.2 Method Blank: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in the sample processing. The method blank is carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.
- 13.3 Laboratory Control Sample (also known as Laboratory Fortified Blank, Spiked Blank, or QC Check Sample): A Sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system.
- 13.4 Matrix Spike (also known as Spiked Sample or Fortified Sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency.
- 13.5 Matrix Spike Duplicate (also known as Spiked Sample or Fortified Sample Duplicate): A second replicate matrix spike prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte.
- 13.6 Laboratory Duplicate: Aliquots of sample taken from the same container under the same laboratory conditions and processed and analyzed under the same conditions but independently.

14.0 REFERENCES

- 14.1 *Standard Methods*, twentieth edition, Method 4500NH₃ D, Nitrogen (Ammonia).

15.0 APPROVAL & ISSUE:

- 15.1 This section indicates which personnel have read, accepted and approved the SOP.

Analyst _____ Date _____

QA Officer _____ Date _____

Technical Director _____ Date _____

SOP #033503: NITROGEN, AMMONIA (NH₃)
 POTENTIOMETRIC, ION SELECTIVE ELECTRODE
 STANDARD METHOD 4500 NH₃ D

Revision: 9
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16.0 TABLES AND FIGURES

16.1 Table 1 Quality Control

16.2 Figure 1: Ammonia Bench Sheet

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<RL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Calibration Standards (1 ppm and 10 ppm)	Yes One each set	90%-110%	Rerun	Notify client. Flag data.
Calibration Check (5 ppm)	Yes One each set	90%-110%	Rerun	Notify client. Flag data.
Laboratory Control Sample (LCS)	Yes One each set	90%-110%	Rerun	Notify client. Flag data.
Control (ERA)	Yes One each set	90%-110%	Rerun	Notify client. Flag data.
Matrix Duplicate	Yes One each set	RPD<20%	Rerun	Notify client. Flag data.
Matrix Spike (MS)	Yes One each set	80%-120%	Rerun	Notify client. Flag data.
Matrix Spike (MSD)	Level 3	RPD<20%	Rerun	Notify client. Flag data.
Dilution & Rerun	No, unless sample out of calib curve range	Is sample now in range?	Yes. Report.	Notify client. Flag data.

Revision: 9
Date: 04/08/11

[illegible]

Exp:
Exp:

SOP #031601: TOTAL DISSOLVED SOLIDS
(Also called: Total Filterable Residue)
METHOD #: 2540C

Revision: 5
Date: 05/25/10

Location: QA Officer's Office
 SOP Files
 TCLP Laboratory
 Solids Laboratory

1.0 Scope

1.1 To describe the method for measuring Total Dissolved Solids (TDS).

2.0 Summary of Method

2.1 An aliquot of sample is taken from a stirring sample and filtered through a filter (pre-weighed filter if TSS is also needed) into a clean side arm flask. After rinsing the solids retained on the filter, the filtrate is quantitatively transferred to a weighed evaporating dish. The sample is then evaporated at 103°C in the oven. Then the dish + solids is moved to a 180°C oven (usually a muffle oven) and dried to a constant weight (usually at least one hour). The weight of solids in the dish represents the TDS.

3.0 Interferences

- 3.1 Poor shaking or stirring can lead to wrong results.
- 3.2 Improper drying of the solids (not to constant weight) will give higher results than the true value.

4.0 Apparatus and Materials

- 4.1 If only TDS is needed use un-weighed glass fiber filters. If TSS is also needed, use Proweigh filters Catalogue number: F934447MM from Environmental Express (phone: 800-343-5319) or www.envexp.com or. Note: if TVSS are to be analyzed TVSS pre-primed (yellow) filters must be used (catalogue number: F93447VOL from Environmental Express). Or the TSS filter can be primed at 550 °C.
- 4.2 Vacuum filtering apparatus compatible with 47 mm glass fiber filters.
- 4.3 25 mL large mouth Pipets
- 4.4 Graduated cylinders: 50 mL, 100 mL.
- 4.5 150 mL aluminum or ceramic evaporating dishes
- 4.6 Oven
- 4.7 Muffle Furnace
- 4.8 Thermometer
- 4.9 Dessicator
- 4.10 Analytical Balance
- 4.11 Vacuum pump
- 4.12 Tweezers

5.0 Reagents

- 5.1 DI Water
- 5.2 LCS from ERA.

6.0 Sample Collection, Preservation and Handling

6.1 The sample is usually a composite sample collected in a plastic or glass liter bottle with no preservation other than refrigeration at 4±2°C. The holding time is 7 days from sample collection.

7.0 Procedure

- 7.1 Record the date, and time of analysis as well as your initials as the analyst on the bench sheet and in the appropriate batch for TDS. A batch is defined as 10 samples of the same or similar matrix.
- 7.2 If TSS is also needed, record the tin number and the filter weight of a preweighed 47 mm glass fiber filter on the TSS bench sheet and record the weight of the evaporating dish on the

SOP #031601: TOTAL DISSOLVED SOLIDS
(Also called: Total Filterable Residue)
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- Merit TDS bench sheet on the line indicating "Blank". If only TDS is needed record only the evaporating dish weight on the TDS bench sheet. Using tweezers place the filter in the filter holder with the wrinkled side up.
- 7.3 Place the filter holder assembly in the clean 150 mL side arm flask with the vacuum hose attached to the side arm.
 - 7.4 Turn on the vacuum and filter 100 ml of deionized water through the filter until all of the water is drawn through. This is the Blank.
 - 7.5 Record the 100 ml volume on the bench sheet(s) for the Blank.
 - 7.6 Then remove the filter, if TSS is needed, and place it in its tin. Then place tin and filter in a drying oven at 103°C for one hour or more. Note: If Filters are dried for more than four hours you can be confident they are dried to constant weight.
 - 7.7 Transfer the filtrate to its weighed evaporating dish and dry in 103°C oven overnight.
 - 7.8 Then move the ceramic evaporating dish to a 180°C oven for at least 1 hour until dried to a constant weight.
 - 7.9 Remove the ceramic evaporating dish from the oven and place it in a desiccator to cool to room temperature.
 - 7.10 Weigh it to the nearest 0.1 mg using an analytical balance.
 - 7.11 Record the weight on the bench sheet for the blank.
 - 7.12 Record on the bench sheet the tin number and the filter weight for another filter and place the preweighed filter in the filter holder assembly with the wrinkled side up, apply vacuum and wet the filter with a little deionized water to ensure adhesion to the holder.
 - 7.13 Record the Merit number on the bench sheet. Then mix a sample by shaking it violently and quickly pour about 150 ml to 250 ml into a plastic cup or beaker.
 - 7.14 Place a Teflon covered magnetic stirring bar in the cup and place the cup on top of a magnetic stirrer. Stir for one minute or more.
 - 7.15 Using a 25 ml serological pipette with a wide opening, remove 25.0 ml of well mixed sample from half way into the cup and halfway between the mixing vortex and the side of the cup. Then drain the pipette onto and through the filter.
 - 7.16 Repeat pipetting (step 16) until 100 ml has been filtered. 50 ml can be used if you know there are a lot of dissolved solids in the sample (from historical testing information).
 - 7.17 Note that shaking vigorously and quickly pouring the sample from the bottle into a graduated cylinder will be a better sampling procedure for some samples. When using this method, pour the sample on to the filter from the cylinder.
 - 7.18 Record the volume you filtered on the bench sheet.
 - 7.19 As you did with the Blank, remove the filter from the filter holder, place it back in its tin for TSS and dry it in a 103°C oven for one hour or more.
 - 7.20 Transfer the filtrate to its weighed evaporating dish and dry it at 103°C overnight. Then dry the dish in a 180°C oven to a constant weight.
 - 7.21 Remove the tin from the oven and cool it to room temperature in a Desiccator. Carefully weigh it on an analytical balance to 0.1 mg.
 - 7.22 Record the weight on the bench sheet.
 - 7.23 Check the dryness of the sample by drying it for another 15 minutes. Then reweigh. The sample is dried to a constant weight if the two weights differ by no more than 4 % or 0.5 mg which ever is less.
 - 7.24 Record the weight on the bench sheet.
 - 7.25 Be sure to perform the QC analyses summarized in Section 8.0.
 - 7.26 Repeat Steps 13 through 24 for each sample.

8.0 Calculations

- 8.1
$$\text{TDS mg/l} = [(\text{Grams of dish} + \text{residue}) - (\text{Grams dish})] / \text{ml sample filtered} \times 1000 \text{ ml/L} \times 1000 \text{ mg/Gram}$$

SOP #031601: TOTAL DISSOLVED SOLIDS
(Also called: Total Filterable Residue)
METHOD #: 2540C

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Date: 05/25/10

9.0 Quality Control

9.1 Also perform the following Quality Control for each sample set. A sample set is a group of one to ten samples run at one time.

Quality Control

QC Sample	Frequency	Acceptable Limits	Corrective Action	Follow up Corrective Action
Blank	1/10 samples	-3 to +3 mg/l	Redry and Reweigh	Reset the entire set of samples with new filters
Laboratory Control Sample-ERA Small Lab Minerals	1/10 samples	Within Supplier's Limits	Redry and Reweigh	Reset the entire set of samples with new filters
Sample Duplicate	1/10 Samples	+/- 20 % of average	Reset sample duplicates	Footnote non- homogeneity
Analytical Balance Check with "S" Weights	1/day	For 1 gram Weight +/- 0.0008 g	Recalibrate Balance and Reweigh	Call for Service
Constant Weight Verification	1/10 samples	4 % or 0.5 mg which ever is smaller	Dry longer and reweigh.	Dry longer and reweigh.

9.0 Documentation

9.1 Total Dissolved Solids Bench sheet

- 9.1.1 Date Started
- 9.1.2 Date Finished
- 9.1.3 Time
- 9.1.4 Analyst
- 9.1.5 Date Checked
- 9.1.6 Checked by
- 9.1.7 Batch #
- 9.1.8 Merit #
- 9.1.9 TSS (Yes/No)
- 9.1.10 Tin #
- 9.1.11 mLs of Sample
- 9.1.12 g Tin
- 9.1.13 g Dry Solids + Tin
- 9.1.14 g Weight after 15 Minutes
- 9.1.15 Ratio: TDS/ Conductivity
- 9.1.16 TDS (mg/L)
- 9.1.17 % Recovery
- 9.1.18 % RPD

9.2 Oven Temperature Log

9.3 TDS/TSS Excel File

10.0References

10.1 *Standard Methods*, twentieth edition, Method 2540C, Solids.

11.0Safety

11.1 Eye protection and gloves must be worn while performing TDS analyses.

SOP #031601: TOTAL DISSOLVED SOLIDS
(Also called: Total Filterable Residue)
METHOD #: 2540C

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- 11.2 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 11.3 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
- 11.4 A reference file of material safety data sheets (MSDSs) is available to all personnel.

12.0 Waste Disposal and Pollution Prevention

- 12.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.
- 12.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

13.0 Approval and Issue

- 13.1 This section indicates which personnel have read, accepted, and approved the SOP. All analysts involved with the SOP should acknowledge their comprehension of the SOP with a signature and a date.

Analyst _____ Date _____

Andy Ball, QA Officer _____ Date _____

Maya V. Murshak, Technical Director _____ Date _____

SOP #034151: PERSULFATE – ULTRAVIOLET OXIDATION METHOD FOR ANALYZING TOTAL ORGANIC CARBON
USING THE DOHRMANN DR-180 CARBON ANALYZER

Revision: 4
Date: 06/19/08

Location: QA Officer's Office
SOP Files
Wet Chemistry Laboratory

1.0 SCOPE

- 1.1 This SOP is for the Persulfate-Ultraviolet Method for analyzing Total Organic Carbon. This SOP is a procedure used by Merit Laboratories for analyzing TOC. This method is applicable to drinking, surface, ground waters & treated mixed wastewater. Reporting limit 1.0 mg/L for water samples.

2.0 SUMMARY OF THE METHOD

- 2.1 This SOP is a procedure for evaluating Total Organic Carbon in liquid samples.
- 2.2 Organic Carbon is oxidized to carbon dioxide, CO₂, by persulfate in the presence of ultraviolet light. The CO₂ produced is measured by a non-dispersive infrared analyzer. Samples are introduced into a continuously gas-purged reactor with ultraviolet lamp and filled with persulfate solution. The CO₂ produced is sparged continuously from the solution and is carried in the gas stream to the infrared detector which is specifically tuned to the absorptive wavelength of CO₂. The area of the peak is calculated and compared to the area of the calibration standard stored in memory and prints out the calibrated organic carbon value in milligrams per liter.

3.0 INTERFERENCES

- 3.1 Excessive acidification of the sample, producing a reduction in pH of the persulfate solution to 1 or less, can result in sluggish and incomplete oxidation of the organic carbon. Highly turbid samples can lead to sluggish or incomplete oxidation as well. Some tannins, lignins and humic acid (complex molecules), may be oxidized slowly because persulfate oxidation is rate-limited. Samples with high chloride content can inhibit oxidation of organic molecules. Samples with greater than 0.1% chloride may prevent oxidation completely. Take care in sampling, handling, and analysis of samples below 1 mg/L, as they can be easily contaminated for trace analysis.

4.0 REAGENTS

- 4.1 Deionized (DI) water
- 4.2 Potassium Acid Phthalate (C₈H₅O₄K) / TOC Standard: Weigh 0.425g (dried) PAP into 100ml volumetric flask, add 60 or 70ml DI water, add 0.1ml concentrated phosphoric acid, bring to volume = 2,000ppm TOC (Store this solution in dark glass under refrigeration and replace monthly).
- 4.3 400 ppm C Standard: Dilute 20ml of 2,000ppm C into a 100ml volumetric flask and bring to volume (Store this solution in dark glass under refrigeration and prepare fresh weekly).
- 4.4 Phosphoric Acid (H₃PO₄) Concentrated
- 4.5 Potassium Persulfate Solution 2%: weigh 10g K₂S₂O₈ into 500ml beaker, add 400ml DI water, 1ml conc. H₃PO₄, dissolve. Pour into 500ml volumetric flask and bring to volume. (Store in a cool dark location. Shelf life is 1 month.
- 4.6 Potassium Persulfate-Mercuric Salt Reagent: This solution is used for samples with high chloride content. Prepare by dissolving 8.2g of reagent grade Mercuric Chloride (HgCl₂) and 9.6g of reagent grade Mercuric Nitrate, monohydrate (Hg (NO₃)₂ · H₂O) in 400ml of DI water and 5 ml concentrated HNO₃. Add 20g of reagent grade Potassium Persulfate. Mix well and make to 1 L with DI water. Prepare monthly.
- 4.7 20% Phosphoric Acid: Dilute 4mls of reagent grade concentrated phosphoric acid to 20mls with the 2% potassium persulfate solution (prepared in 4.5).
- 4.8 Oxygen tank
- 4.9 Control ERA / TOC

5.0 APPARATUS & MATERIALS

- 5.1 Dohrmann DC-180 Carbon Analyzer

- 5.2 50ml centrifuge tubes with screw caps
- 5.3 100ml volumetric flasks
- 5.4 500ml volumetric flask

6.0 SAMPLE HANDLING AND PRESERVATION

- 6.1 Samples should be collected in amber glass bottles with TFE-lined cap and acidified to a pH \leq 2 with H₂SO₄. Regulatory storage is 28 days under refrigeration (4 degrees C) and acidified.

7.0 PROCEDURE

7.1 DAILY STARTUP

- 7.1.1 Check to see that UV reactor is filled with reagent.
- 7.1.2 Make sure there is enough persulfate reagent in supply bottle to last through at least a day's operation.
- 7.1.3 Check to make sure Gas/Liquid separator is half filled with water. On a daily basis, the pH of the G/L liquid should be checked. A pH of less than 3 is necessary for maximum sparging efficiency.
- 7.1.4 Ensure water trap is less than half-full with water.
- 7.1.5 Make sure all plumbing is properly connected. Re-connect the Teflon line from the UV reactor and the G/L separator.
- 7.1.6 Check to see that waste container is empty.
- 7.1.7 Make sure the acid bottle has sufficient acid
- 7.1.8 Check to see that you have sufficient oxygen for the day's operation.

7.2 SYSTEM ON

- 7.2.1 Verify that the main power is on and that the system main menu is being displayed.
- 7.2.2 From "System On/Off" menu ([= / -] [1]), select "O₂/ UV/ Pump On".
- 7.2.3 Observe UV lamp is on, gas is bubbling in both the UV vessel and the G/L separator and the peristaltic pump is on.
- 7.2.4 Check each pump channel closely. Verify proper fluid movement through each line and replace any worn or weakly-pumping tubings. Refer to section 3.5 of manual for pump pressure adjustments.
- 7.2.5 Check the flow rate out the NDIR. Refer to the Gas Flow Rate Checks in section 3.5 of manual and verify proper gas flow rates for all modes you will be using.
- 7.2.6 From "Main Menu", select "Monitor baseline". Observe for stable baseline before starting an analysis.

7.3 INITIAL SET-UP

- 7.3.1 From "Analysis Modes" menu, ([+ / -] [2] [3]), select NPOC [1] (non-purgable organic carbon) (In most surface and ground waters the POC contribution is negligible. Therefore, in practice, the NPOC determination is substituted for TOC). Direct Inject NPOC (Y/N)? Press [No], NPOC w/Inj Loop.
- 7.3.2 Check attachment for sequence times and sampling parameters for NPOC.
- 7.3.3 From the "Main Menu" select "Monitor Baseline" [5].
- 7.3.4 Observe baseline in the bottom right corner of the screen. The system will be ready for calibration or analysis when the baseline becomes stable.

7.4 CALIBRATION

- 7.4.1 A calibration curve must be created once every year.
- 7.4.2 From "Calibration Mode" menu ([+ / -] [2] [4]), select the NPOC w/ inject loop mode [1]. When [1] is selected, the appropriate volume (0.2ml) is displayed with a blinking cursor at the bottom of the screen. If the loop size is correct, press [ENTER]; otherwise, use [CLEAR] to erase the line and enter correct volume in ml and then press [ENTER].
- 7.4.3 Submerge sample pick-up line into container that has the standard solution of interest (400ppm TOC standard).
- 7.4.4 Press [CAL], enter the ppmC standard concentration (400), being used and then press [ENTER].

- 7.4.5 After “Run Conditions” are printed, if ready, press [YES]. [NO] will exit from CAL mode and return the main menu.
- 7.4.6 The CAL factor for the mode selected will be automatically adjusted at the end of the analysis. Compare the results obtained with Table 5.5.1 of the manual. If your value falls outside the expected range, double-check your gas flow rate and pump tubes flows. If o.k., the baseline may not have been stable. Try calibrating again.
- 7.4.7 Expected raw count range for 0.2ml injection loop volume and 400ppm concentration is between 768000-1280000.
- 7.4.8 * Gas flow rate is approximately $200 \pm$ cc/min.
- 7.5 SAMPLE RUN
 - 7.5.1 An analysis can be started anytime after the baseline becomes stable. Usually a 30-minute warm-up time is used.
 - 7.5.2 Always start a sample set with a blank (DI) and verify calibration with a standard (10ppm). (Use the calibration update function to make minor adjustments to the calibration factor, if necessary).
 - 7.5.3 Mix sample bottle and pour approximately 50ml into plastic centrifuge tube.
 - 7.5.4 Submerge sample pick-up line into centrifuge tube. Press [RUN] , enter ID#, Press [ENTER]. Sample run is approximately 7 minutes.
 - 7.5.5 After sparging begins the pick-up line can be placed back into DI bottle to rinse line clean of sample.
 - 7.5.6 The detector will calculate Cppm and display result.
 - 7.5.7 If a sample contains a high concentration of TOC (> 50ppm), a DI blank is usually run between samples.

8.0 MAINTENANCE AND TROUBLESHOOTING

8.1 DAILY CHECKS

- 8.1.1 Oxygen supply
- 8.1.2 Persulfate supply
- 8.1.3 Acid supply
- 8.1.4 Printer paper supply
- 8.1.5 Check Cu and Sn scrubber
- 8.1.6 Check pH of G/L separator (< 3), add drop of concentrated phosphoric if not.
- 8.1.7 Connect output line on UV vessel to top port of GLS.
- 8.1.8 Printer on; O₂, UV vessel and pump on [+/-] [1] [1].
- 8.1.9 Carrier gas flow rate (approx. 200 cc/min.
- 8.1.10 Steady baseline [+/-] [5].

8.2 WEEKLY CHECKS

- 8.2.1 Daily checks, plus
- 8.2.2 Check liquid flow rate – pump tubing conditions.
- 8.2.3 Check for moisture in the LiOH tube.
- 8.2.4 Check for injection port septum if syringe analysis is used regularly.

8.3 BI-MONTHLY CHECKS

- 8.3.1 Daily and weekly checks, plus
- 8.3.2 Change pump tubings. (inspect for ware)

Questions on instrument operation can be found in DC-180 Operation Manual.

9.0 QUALITY CONTROL

9.1 See Table 1

9.2 A sample batch will consist of 20 samples or less. The QC samples that are analyzed per batch are:

- Method Blank
- Blank Spike
- Control (ERA or another outside known)

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Revision: 4
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- LCS
- Matrix Spike
- Matrix Spike Dup (level 3 QC or requested)
- Matrix Duplicate

9.3 A Blank Spike, Matrix Spike, Matrix Duplicate are run every 10 samples.

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	
Laboratory Control Sample (LCS) Soluble or insoluble	Yes One every 20 samples	85%-115%	Rerun	
Matrix Duplicate	Yes One each 10 samples	RPD<20%	Rerun entire set	
Matrix Spike	Yes One each 10 samples	85%-115%	Analyze by Method of Standard Additions	
Matrix Spike Duplicate	Level 3 One every 10 samples			
Dilution & Rerun	No except if result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	

10.0 DOCUMENTATION

- 10.1 DC-180 Carbon Analyzer raw data printout
- 10.2 TOC Bench book
- 10.3 DC-180 Carbon Analyzer Maintenance Log

11.0 METHOD PERFORMANCE

- 11.1 Precision and accuracy studies are performed on as needed basis.
- 11.2 Method Detection Limit studies are performed annually.

12.0 REFERENCES

- 12.1 *Standard Methods*, twentieth edition, Method 5310C, Total Organic Carbon (TOC).

13.0 APPROVAL & ISSUE:

- 13.1 The following personnel have read, accepted and approved this standard operating practice.

Analyst Date

Andy Ball, QA Officer Date

Maya V. Murshak, Technical Director Date

Location: QA Officer's Office
pH laboratory
SOP Files

1.0 SCOPE

- 1.1 To measure pH in water samples.

2.0 SUMMARY OF METHOD

- 2.1 This SOP is designed to measure the pH of water samples. The procedure in this method is written for the Hach SensION3 Laboratory pH Meter (P/N 51750-18). This SOP follows EPA method 4500 H⁺ B.

3.0 INTERFERENCES

- 3.1 Temperature can be an interference. Temperature can change the acid-base equilibrium constant.
- 3.2 Carbon Dioxide absorption from the atmosphere. This can form carbonic acid in water, which can cause interferences.
- 3.3 A pH above 10 can have sodium interference.

4.0 APPARATUS AND MATERIALS

- 4.1 Hach SensION3 Laboratory pH Meter (P/N 51750-18).
- 4.2 Platinum Series Combination pH Electrode with Temperature (Cat. #: 51910-00)
- 4.3 Potassium Chloride Electrolyte Cartridge (Cat.#: 25469-02)
- 4.4 Stir Plate
- 4.5 Magnetic Stir Bar
- 4.6 Plastic Cup
- 4.7 Paper Towel
- 4.8 50 mL Centrifuge Tubes

5.0 REAGENTS

- 5.1 pH, 4.00, color-coded red
- 5.2 pH, 7.00, color-coded yellow
- 5.3 pH, 10.00, color coded blue
- 5.4 pH, 5.00, color coded clear (Laboratory Control Sample), Micro Essential Lab Hydriion Products prepared by adding 1 pill per 100mL of DI Water
- 5.5 pH, 2.00, color coded clear, , Micro Essential Lab Hydriion Products prepared by adding 1 pill per 100mL of DI Water

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

- 6.1 pH analyses must be run as soon as possible after sample collection. The samples must be stored in an unpreserved plastic container.

7.0 PROCEDURE

- 7.1 Turn on the meter.
- 7.2 Inspect the Potassium Chloride Electrolyte Gel Cartridge to ensure that it is not empty. If it is empty replace it.
- 7.3 Prime the electrode by pushing the dispenser until gel comes out of the reference junction. Rinse excess gel from the tip and the outlet with deionized (DI) water.
- 7.4 Press the <CAL> button on the meter. The display will prompt for Standard 1 (pH= 7.00).
- 7.5 Place the electrode into fresh pH=7 buffer. Then press <Read/Enter> and stir until the display reads "pH STD 2. "Fresh" is defined as prepared within 7 days of calibration.
- 7.6 Remove the electrode from the pH=7 buffer and rinse it well with DI water, dry with a paper towel.

- 7.7 Place the electrode into pH=4 buffer. Stir and press <Enter>. Wait until the display prompts for STD 3, then press exit. This is a two point calibration.
- 7.8 The Slope and "Store?" will appear. If the slope is $-58 \pm 3 \text{ mV/pH}$ Unit record it along with the pH readings of the two buffers on the bench sheet. If the slope is out of this range press <Exit> and recalibrate. Then press <Read/Enter> to save the calibration.
- 7.9 Remove the electrode from the buffer, rinse well with DI water and dry with a paper towel. The display will now automatically switch to the pH reading mode (i.e. "4.00 pH").
- 7.10 Place the electrode into pH=10 buffer, stir and wait until the reading is stable. The display must show 10.00 ± 0.05 pH units. Record this value on the bench sheet. If it is out of this range recalibrate until it reads in this range. Calibration is now complete. Recalibrate every 10 samples or every day whichever comes first.
- 7.11 Remove the electrode, rinse well with DI water, pat dry with paper towel, and place it into the Laboratory Control Sample (LCS).
- 7.12 Stir and wait for a stable pH reading on the display. Ensure that the pH reading for the LCS is within the certified acceptance range.
- 7.13 Remove the electrode, rinse well with DI water. Place the electrode into the sample and stir. Wait until the display shows a stable pH reading and the sample has a temperature near ($\pm 5^\circ\text{C}$) the temperature of the buffers (room temperature).
- 7.14 Record all buffer readings, LCS, sample and sample duplicate readings as well as the temperature displayed on the small monitor in the pH bench book along with the Merit Sample Number, the date and your initials.
- 7.15 Replace the sample with a new aliquot and repeat the test (duplicate analysis).
- 7.16 Note that the samples and the pH buffers used for calibrating the instrument must be close to the sample temperature ($\pm 5^\circ\text{C}$).
- 7.17 After samples are tested. Read the LCS buffer at the end to ensure that the meter remained in calibration. If it reads beyond the range $\text{pH}=5 \pm 0.05$ recalibrate and reread the samples.
- 7.18 To increase accuracy perform a calibration check at least every 10 samples. Recalibrate as needed.
- 7.19 Remove the electrode, rinse well with DI water, pat dry with a paper towel and place it in the overnight beaker containing East Lansing, MI tap water.

8.0 QUALITY CONTROL

- 8.1 All QA/QC information that needs to be analyzed are listed in the "Quality Control Requirements" table below.
- 8.2 This table also includes acceptable upper and lower limits, any corrective actions not specified in the procedures.

Quality Control Requirements

QC Work Task	Frequency	Acceptance Range	Corrective action
Calibration with two Std buffers (pH=7 & 4) plus third Std buffer (pH=10) verification	1/day and when calibration check is outside acceptance range	± 0.05 of pH Slope = $-58 \pm 3 \text{ mV/pH unit}$	1. Clean electrode and reference junction. Then recalibrate. 2. Prepare new buffers and recalibrate. 3. Call for service.
Laboratory Control Sample	1/day or every 10 samples	Within certified range	Same as for calibration above.
Temperature of samples and Buffers	Record with each pH reading	Within $\pm 5^\circ\text{C}$ of the buffers (room temperature)	Hold at room temperature until within acceptable range.
Calibration check buffer pH 2.00 and pH 5.00	1/set or every 10 samples	± 0.05 pH units	Recalibrate and rerun samples read since the last acceptable calibration check.
End calibration check Read one standard	1/set or 1/day	± 0.05 pH units	Recalibrate and rerun samples read since the last acceptable calibration check

9.0 DOCUMENTATION

9.1 pH Bench book that records the following information:

- 9.1.1 Date of Standards Made, Expiration, and Calibration Value
- 9.1.2 Calibration information (buffer used, value read)
- 9.1.3 LCS values
- 9.1.4 Calibration Check
- 9.1.5 Lot #'s for Buffer Solutions
- 9.1.6 Calibration Slope Value
- 9.1.7 Merit ID Number
- 9.1.8 Date
- 9.1.9 pH Measured
- 9.1.10 Temperature at which the pH is measured
- 9.1.11 Matrix
- 9.1.12 Analyst Initials

10.0 METHOD PERFORMANCE

- 10.1 This method is evaluated by the blinds performed every quarter. If the pH values are not within the acceptable criteria, a the matter is investigated and a corrective plan is determined.

11.0 REFERENCES

- 11.1 *Standard Methods*, twentieth edition, Method 4500-H⁺ B.

12.0 SAFETY

- 12.1 Eye protection and gloves must be worn while performing pH analyses.
- 12.2 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 12.3 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
- 12.4 A reference file of material safety data sheets (MSDSs) is available to all personnel.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

13.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.

13.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.0 APPROVAL & ISSUE

14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

Analyst _____ Date _____

Andy Ball, QA Officer _____ Date _____

Maya V. Murshak, Technical Director _____ Date _____

Location: QA Officer's Office
SOP Files
Wet Chemistry Laboratory

1.0 SCOPE

- 1.1 This SOP is applicable to drinking, surface, and saline water, domestic and industrial wastes, and acid rain (atmospheric deposition). Conductivity is run by EPA Method 120.1.

2.0 SUMMARY OF THE METHOD

- 2.1 This SOP is a procedure for evaluating Conductivity in liquid samples.
- 2.2 The specific conductance of a sample is measured by use of a self-contained conductivity meter.
- 2.3 Samples are preferably analyzed at 25°C.
- 2.4 Field measurements with comparable instruments are reliable.

3.0 INTERFERENCES

- 3.1 N/A

4.0 APPARATUS AND MATERIALS

- 4.1 Hach Conductivity/TDS Meter
- 4.2 1 L Volumetric flask
- 4.3 Plastic 50 mL Centrifuge tubes
- 4.4 Clean plastic cup
- 4.5 Pipette
- 4.6 Graduated Cylinder
- 4.7 Analytical Balance, 0.03 g – 100 g capacity

5.0 REAGENTS

- 5.1 Deionized (DI) water
- 5.2 Sodium Chloride (NaCl)
- 5.3 ERA Standard (2nd Source), see Certified Reference Material for preparation and concentration

6.0 SAMPLE HANDLING AND PRESERVATION

- 6.1 Conductivity is best analyzed as soon as possible from the time the sample is collected. Maximum holding time for water samples is 14 days when refrigerated at 4°C ± 2°C.
- 6.2 Samples must be provided in unpreserved, clear plastic bottles.
- 6.3 Analyses can be performed either in the field or laboratory.

7.0 PROCEDURE

7.1 PREPARATION OF STANDARD SOLUTIONS, PREPARED FRESH EVERY 2 MONTHS

- 7.1.1 For a 180-µmhos/cm standard, dissolve 0.0214 g NaCl in 250 mL of DI water. The 180-µmhos/cm standard is used for blank spike.
- 7.1.2 For a 1,990-µmhos/cm standard, dissolve 0.25 g NaCl in 250 mL of DI water. The 1,990-µmhos/cm standard is used for Laboratory Control Sample (LCS).

7.2 MEASUREMENT

- 7.2.1 Turn on meter and place probe in a plastic cup filled with DI water.
- 7.2.2 For a blank, pour 10 mL DI water in a centrifuge tube.
- 7.2.3 Rinse off probe then place in tube. Make sure to eliminate all air bubbles around the tube. Press the 2 key for the most sensitive reading possible.
- 7.2.4 Place probe back in cup containing clean DI water.
- 7.2.5 Pour 10 mL of Blank Spike into centrifuge tube and read conductivity by following Section 7.2.3. Rinse off probe between each sample.
- 7.2.6 Pour 10 mL of LCS into centrifuge tube and read conductivity by following Section 7.2.3. Rinse off probe between each sample.
- 7.2.7 Pour 10 mL of Control, ERA standard, into centrifuge tube and read conductivity by following Section 7.2.3. Rinse off probe between each sample.
- 7.2.8 Pour 10 mL sample in another tube. Rinse off probe and place in this tube just as before. Adjust settings if the meter is reading too sensitively by pressing the 20 key.

If the meter still reads a value too high, press the 200 key. The meter gives values in $\mu\text{mhos/cm}$.

8.0 QUALITY CONTROL

8.1 See Table 1

8.2 Samples are analyzed in batches of twenty (20) or less per QC set. The QC samples that are analyzed per batch are:

- Control
- LCS
- Duplicate
- Method Blank
- Blank Spike

9.0 DOCUMENTATION

9.1 Conductivity Bench sheet

- 9.1.1 Analyst
- 9.1.2 Date Run
- 9.1.3 Method #
- 9.1.4 Detection Limit
- 9.1.5 Program #
- 9.1.6 Wavelength
- 9.1.7 Merit #
- 9.1.8 Dilution
- 9.1.9 Umhos/cm
- 9.1.10 ABS
- 9.1.11 %S
- 9.1.12 Result (umhos/cm)
- 9.1.13 Spike (umhos/cm)
- 9.1.14 % Recovery
- 9.1.15 Lot/ Source
- 9.1.16 Run Time

10.0 METHOD PERFORMANCE

10.1 Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.)

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation)	Yes	1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Blank	One each set			
Blank Spike	Yes	90%-110%	Rerun	Notify client. Flag data.
	One every 10 samples			
Control	Yes	90%-110%	Rerun	Notify client. Flag data.
	One every 10 samples			
Laboratory Control Sample (LCS)	Yes	90%-110%	Rerun	Notify client. Flag data.
	One each set			
Matrix Duplicate	Yes	RPD<20%	Rerun entire set	Notify client. Flag data.
	One each set			

11.0 REFERENCES

- 11.1 EPA Water NPDES, Method 120.1, EPA Test Methods, Revision 1982, Conductance (Specific Conductance, μmhos at 25°C).

12.0 SAFETY

- 12.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 12.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
- 12.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

- 13.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.
- 13.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.0 APPROVAL & ISSUE:

- 14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP should acknowledge their comprehension of the SOP with a signature and a date.

Analyst _____ Date _____

Andy Ball, QA Officer _____ Date _____

Maya V. Murshak, Technical Director _____ Date _____

SOP #033354: PYRIDINE-PYRAZALONE COLORIMETRIC METHOD FOR ANALYZING CYANIDE USING THE DR/4000 HACH SPECTROPHOTOMETER

Revision: 9
Date: 05/09/08

Location QA Director's Office
 Wet Chemistry Laboratory

1.0 SCOPE AND APPLICATION

1.1 This SOP is for the Colorimetric method for analyzing cyanide after full distillation using the Lachat micro-dist system. This SOP is a procedure used by Merit for analyzing cyanide after distillation. This method is applicable to drinking, wastewater, groundwater, sea water and solid matrices. Reporting limit 0.005 mg /l for water samples using double distillation. The reporting limit for solids is 0.5 mg/kg.

2.0 SUMMARY OF METHOD

2.1 Cyanide is analyzed after distillation using the DR-4000 Hach spectrophotometer, Method Code 8027. Three separate reagents are added to a distilled neutralized sample. The pyridine-pyrazolone indicator that is used gives an intense blue color if cyanide is present (starts out as pink then goes blue. Reaction time after adding reagents is 30 minutes.

3.0 INTERFERENCES

- 3.1 If the display flashes 0.200, the upper limit of the pre-calibrated range has been exceeded and a sample dilution is needed. A flashing value of -0.020 indicates the sample has a negative absorbance value relative to the blank. This negative value indicates a possible interference in the water sample or a procedure error by the user. Small negative values probably are due to small variations between sample cells or amounts of reagent added and should be treated as a concentration value of zero.
- 3.2 Delaying the addition of the CyaniVer 5 Reagent Pillow for more than 0.5minutes after addition of CyaniVer 4 will give lower test results. It is not essential that all of the CyaniVer 4 reagent be dissolved before proceeding with the addition of CyaniVer 5.
- 3.3 Too much chlorine will cause a milky white precipitate after addition of CyaniVer 5. See CN- Lachat Distillation SOP for pre-distillation treatment of samples.

4.0 APPARATUS AND MATERIALS

- 4.1 DR/4000 Hach Spectrophotometer (wavelength knob to 612 nm)
- 4.2 10 mL sample cells
- 4.3 10 mL sample cells adapter
- 4.4 25 mL clear glass vials
- 4.5 Scale (American Scientific / Conventional lab.)
- 4.6 Pasteur pipets / pipet bulbs
- 4.7 100ml volumetric flask (2)
- 4.8 0.1 –1.0ml auto-pipettor / tips
- 4.9 10ml pipets
- 4.10 50ml plastic centrifuge tubes

5.0 REAGENTS

- 5.1 CyaniVer 3 powder pillows for 10 mL sample. (Contains: Sodium Phosphate Dibasic, Halane, & Potassium Phosphate, Monobasic). Shelf life for CyaniVer 3,4&5 is 5 years at 10-30 degrees C.
- 5.2 CyaniVer 4 powder pillows for 10 ml sample. (Contains: Ascorbic Acid, Pyridine-3-nitrophthalic acid, & Sodium Sulfate)
- 5.3 CyaniVer 5 powder pillows for 10ml sample. (Contains: Potassium Phosphate, Monobasic, Sodium Sulfate, 3-Methyl-1-phenyl-2pyrazolin-5-one, & Sodium Phosphate Dibasic.)
- 5.4 Stock cyanides standard 1,000 mg/L CN⁻: Weigh 0.251 g of Potassium cyanide (KCN⁻) onto weighing paper or into a beaker. Add KCN⁻ from weighing paper to 100mL volumetric flask being careful not to lose any of NaCN⁻. Add 50ml DI water. Pipet 1 ml of 1N NaOH into flask using auto-pipettor. Bring to final volume of 100ml. Prepare fresh weekly. Refrigerate.
- 5.5 10ppm working standard: Pipet 1ml of 1,000ppm into 100ml volumetric flask using auto-pipettor. Bring to final volume of 100ml. Prepare fresh with each new sample batch. Refrigerate.

SOP #033354: PYRIDINE-PYRAZALONE COLORIMETRIC METHOD FOR ANALYZING CYANIDE USING THE DR/4000 HACH SPECTROPHOTOMETER

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- 5.6 Distilled water.
- 5.7 2.5 N HCl : 250ml / 52ml concentrated HCL. Used for neutralization. *See Wet Chem Reagent Prep Log*
- 5.8 Phenolphthalein indicator: weigh 0.125g phenolphthalein on weighing paper and transfer to 25ml volumetric flask. Pipet 12.5ml of DI water and 12.5ml of ACS Grade isopropyl alcohol to volumetric flask. Mix. *See Wet Chem Reagent Prep Log*
- 5.9 1N NaOH : Weigh 8.0g NaOH pellets into a 250ml plastic bottle. Add 200ml DI water to bottle using scale. *See Wet Chem Reagent Prep Log.*
- 5.10 0.5N HCl : Pipet 10ml of 2.5N HCl into a 50ml centrifuge tube and bring to 50ml final volume using the scale. *See Wet Chem Reagent Prep Log*
- 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING
- 6.1 Water samples are collected in plastic containers and preserved with NaOH to a pH at 12.
- 6.2 Soil samples are collected in a non preserved glass container.
- 6.3 Holding time for cyanide is 14 days from the time of sampling.
- 7.0 PROCEDURE^[1]
- 7.1 Allow for DR/4000 warm-up (approximately 15 min.)
- 7.2 All samples including QC samples having been distilled, neutralized, and brought to final volume (10 mL) in the 15ml glass vials are now ready to be analyzed. It is possible to do two samples at a time. Start with method blank, which is used to zero instrument.
- 7.3 Add the contents of one CyaniVer 3 reagent pillow to each sample vial, stopper and shake for 0.5 minutes—press: 0.5 timer. When timer goes off, reset timer for 0.5 and allow samples to stand undisturbed.
- 7.4 After the timer sounds, add the contents of a CyaniVer 4 reagent pillow to each sample, re-stopper and shake for 0.1 minute—press timer. When timer sounds, immediately add CyaniVer 5 reagent pillow and shake vigorously to dissolve. Set timer for 30 minutes. Repeat procedure for all the samples. *See 3.2.*
- 7.5 The cyanide calibration curve needs to be entered in the DR/4000.
- 7.6 Select user program **175** ; calibration curve & wavelength 612 nm are then auto selected. Place the 10 mL vial adapters into cell compartment making sure openings are aligned with light path in compartment.
- 7.7 When 30-minute reaction period is over pour method blank into 10ml sample cell, cap the cell and place into cell compartment with letter on cell facing the front.
- 7.8 Press: **Zero** Absorbance so displays reads 0.000. Enter the entire calibration curve.
- 7.9 Press 0.000 Std 1, which is Absorbance, then Press 0.000 Std 2, which is the corresponding concentration to that Absorbance.
- 7.10 Repeat this procedure with the 6 calibration points of the curve. Once the curve is entered, press: **Best Fit Calculate** and then press: **Conc.** The Cyanide Calibration curve is now ready.
- 7.11 Pour samples into 10ml cell and place into cell compartment and read samples mg CN-/L directly from display. Record reading in Cyanide bench book.
- 7.12 Calculation:

$$\text{mg CN}^- = \frac{\text{mg}}{\text{L}} \text{ from display} \times \frac{\text{Final Volume (ml)}}{\text{Sample Volume or Weight (ml / g)}}$$

Example = spectro reading 0.041 mg/L x 10 mL/5 mL = 0.082 mg/L

^[1] Lachat Instruments Micro-Dist Distillation system Reference & Methods Manual.
Reference Method: EPA Method 335.4.

SOP #033354: PYRIDINE-PYRAZALONE COLORIMETRIC METHOD FOR ANALYZING CYANIDE USING THE DR/4000 HACH SPECTROPHOTOMETER

Revision: 9
Date: 05/09/08

8.0 QUALITY CONTROL

- 8.1 QC is analyzed per matrix per batch of 20 samples or less
- 8.2 6 point calibration curve (see attached curve with Lachat distillation SOP)
 - 8.2.1 A new calibration shall be run once every 6 months.
- 8.3 Each QC set must include the following:
 - 8.3.1 Standard Check (Blank Spike or ICV)
 - 8.3.2 LCS
 - 8.3.3 Method Blank
 - 8.3.4 Reagent Blank
 - 8.3.5 Duplicate (DUP)
 - 8.3.6 Matrix Spike (MS)
 - 8.3.7 Matrix Spike Duplicate (MSD) – optional
 - 8.3.8 A set of 6 calibration standards, ranging from 0.005 – 0.200 mg/l is run exactly the same as samples.
 - 8.3.9 A calibration coefficient of 0.999 or greater is necessary for working calibration curve. If less than 0.999 then rerun.
 - 8.3.10 For each sample batch the calibration curve is verified with an initial calibration verification (ICV) and a continuing calibration verification (CCV) every 10 samples and at the end of a run.

9.0 Documentation

- 9.1 Maintain bench sheet with calibration curve, QC data, sample data, method number, date of analysis, analyst name and detection limit.

10.0 METHOD PERFORMANCE

- 10.1 Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.)
- 10.2 Method Detection limit studies are performed annually.

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and re-digest samples.	Notify client. Flag data.
Laboratory Control Sample (LCS) Soluble or insoluble	Yes 1/20 samples	90%-110%	Re-digest the sample set.	Notify client. Flag data.
Continuing Calibration Verification (CCV)	Yes 1/10 samples	90%-110%	All samples bracketed by a CCV outside the acceptable control limits must be re-digested and re-analyzed.	Notify client. Flag data.
Matrix Duplicate	Yes 1/20 samples 1/10 samples for Drinking water samples	RPD<20%	Re-digest samples and QC.	Notify client. Flag data.
Matrix Spike	Yes 1/ 20 samples	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Matrix Spike Duplicate	Level 3 One every 20 samples			Notify client. Flag data.

**SOP #033354: PYRIDINE-PYRAZALONE COLORIMETRIC METHOD FOR ANALYZING
CYANIDE USING THE DR/4000 HACH SPECTROPHOTOMETER**

Revision: 9
Date: 05/09/08

Dilution & Rerun	No except if result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	Notify client. Flag data.
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11.0 SAFETY

11.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

11.2 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

11.2.1 Hydrochloric acid

11.2.2 Silver nitrate

11.2.3 Potassium cyanide

11.2.4 Sulfuric acid

11.3 Because of the toxicity of evolved hydrogen cyanide (HCN), distillation should be performed in a well vented hood.

12.0 REFERENCES

12.1 Method 335.4, Revision 1.0, 1993

13.0 APPROVAL & ISSUE:

Jeff Phiifer, Senior Analyst

Date

Andy Ball, QA Officer

Date

Maya Murshak, Technical Director

Date

Location: QA Officer's Office
SOP Files
Wet Chemistry Laboratory

1.0 SCOPE

- 1.1 This SOP is applicable to drinking, surface, and saline waters. This procedure is based on method by HACH which states not approved for EPA reporting.

2.0 SUMMARY OF THE METHOD

- 2.1 This SOP is an spectrophotometric procedure for evaluating Turbidity in liquid samples.

3.0 INTERFERENCES

- 3.1 Presence of floating debris and coarse sediments that settle out rapidly will give low readings. Finely divided air bubbles will affect results in a positive manner.

4.0 APPARATUS AND MATERIALS

- 4.1 100 mL volumetric flask
- 4.2 Hach DR/3000 Spectrophotometer
- 4.3 2 clean cuvettes
- 4.4 Parafilm
- 4.5 Pipettes
- 4.6 Volumetric Flask

5.0 REAGENTS

- 5.1 Deionized (DI) water
- 5.2 Hydrazine Sulfate
- 5.3 Hexamethylenetetramine

6.0 SAMPLE HANDLING AND PRESERVATION

- 6.1 Turbidity is best analyzed as soon as possible from the time the sample is collected. Maximum holding time is 48 hours refrigerated at $4\pm 2^{\circ}\text{C}$.
- 6.2 Samples must be provided in unpreserved, clear plastic bottles.

7.0 PROCEDURE

7.1 Preparation of Standard Solution

- 7.1.1 Stir together 10.0 mL DI Water, 0.500 g Hydrazine Sulfate and 0.050 g Hexamethylenetetramine in a 100 mL volumetric flask until all particles are dissolved in the water.
- 7.1.2 Seal tightly with parafilm and leave it sit in a protected place overnight.
- 7.1.3 Bring standard solution to 100 mL before use.

7.2 Color Development and Measurement

- 7.2.1 Select the stored program for Turbidity by pressing 5 and 9 with the numeric keys and the Stored Program key then press enter.
- 7.2.2 Turn the wavelength dial to 450 nm.
- 7.2.3 Place 25.0 mL of sample in a 25 mL cuvette. If the sample is highly colored, dilute as needed. The upper limit for this analysis is 660 Formazin Turbidity Units (FTU).
- 7.2.4 Prepare a Blank by putting 25.0 mL of DI water in another cuvette.
- 7.2.5 Place the Blank in the spectrophotometer so as the 25 mL mark faces forward. Close the light shield.
- 7.2.6 Press the ZERO and then CONC keys. The spectrophotometer is zeroed for the analysis.
- 7.2.7 Place the sample into the cell holder and close the light shield. Results will be displayed in Formazin turbidity units (FTU).

8.0 QUALITY CONTROL

- 8.1 See Table 1

8.2 Samples are analyzed in batches of 20 or less per QC set. The QC samples that are analyzed per batch are:

- Standard Check
- LCS
- MS
- DUP
- MSD (optional)
- Method Blank

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify client. Flag data.
Laboratory Control Sample (LCS)	Yes One every 20 samples	90%-110%	Rerun	Notify client. Flag data.
Matrix Duplicate	Yes One each set	RPD<20%	Rerun entire set	Notify client. Flag data.
Matrix Spike	Yes One each set	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Matrix Spike Duplicate	Yes One every 20 samples Level III	80%-120%	Analyze by Method of Standard Additions	Notify client. Flag data.
Dilution & Rerun	No except if result indicates suppressive interference	Does interference persist?	Yes. Rerun with Method of Standard Additions	Notify client. Flag data.

9.0 DOCUMENTATION

9.1 Turbidity Bench Sheet

- 9.1.1 Analyst
- 9.1.2 Analysis
- 9.1.3 Date Run
- 9.1.4 Detection Limit
- 9.1.5 Wavelength
- 9.1.6 Merit #
- 9.1.7 Dilution
- 9.1.8 Concentration (FTU)
- 9.1.9 Result
- 9.1.10 Spike Concentration
- 9.1.11 % Recovery
- 9.1.12 Batch ID

10.0 METHOD PERFORMANCE

10.1 Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.)

10.2 Method Detection limit studies are performed annually.

11.0 REFERENCES

- 11.1 EPA Water NPDES, Method 180.1, EPA Test Methods, Revision 1982, Turbidity (Nephelometric).
- 11.2 Hach DR/3000 Spectrophotometer Manual.

12.0 SAFETY

- 12.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
- 12.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
- 12.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.

13.0 WASTE DISPOSAL AND POLLUTION PREVENTION

- 13.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.
- 13.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

14.0 APPROVAL & ISSUE

- 14.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP must acknowledge their comprehension of the SOP with a signature and a date.

Analyst _____ Date _____

Andy Ball, QA Officer _____ Date _____

Maya V. Murshak, Technical Director _____ Date _____

SOP Log

	<u>Finished?</u>	<u>Written By</u>	<u>Last Revised</u>	<u>SOP Number</u>	<u>Revision #</u>
<u>Administrative</u>	00				
Archival of Electronic Data	X	Pat Q.	10/27/09	000001	3
Complaints	X	Maya M.	05/17/10	000002	2
Electronic Deliverables	X	Maya M.	10/27/09	000003	3
Faxing	X	Rosanne A.	10/26/09	000004	3
Invoice	X	Paula S./Barb R.	10/25/09	000005	2
Method Validation	X	Mike G.	02/19/02	000006	1
Phone System	X	Mike G.	10/23/09	000007	2
QA Manual Updates	X	Maya M.	10/29/09	000008	3
Reports	X	Paula S./Barb R.	10/26/09	000009	3
Sending Reports/Invoices	X	Paula S./Barb R.	10/21/09	000010	4
How to Write SOPs	X	Maya M.	10/26/09	000011	6
Training Records	X	Mike G./Maya M.	10/27/09	000012	2
Validation	X	Maya M.	09/17/00	000013	2
Changing SOPs	X	Chris D.	10/21/09	000014	2
Document Control	X	Chris D.	10/21/09	000015	2
Sample Custody and Data Flow	X	Chris D.	10/07/09	000016	2
Visitors	X	Chris D.	10/21/09	000017	2
Internal Audits	X	Chris D.	07/19/10	000018	3
SOP Distribution	X	Chris D.	10/27/09	000019	2
Standard Tracking	X	Joesph K.	11/03/05	000020	1
CRA-GM-Remediation	X	GM	02/23/05	000021	1
Data Integrity	X	Joesph K	10/21/09	000022	2
Flow of Consumable Materials	X	Paula S./Barb R.	05/18/10	000023	3
Ordering Reagents and Supplies	X	Kara T./Violetta M.	06/29/10	000024	3
Chain of Custody Preparation	X	Paula S./Barb R.	10/26/09	000025	2
<u>Sample Handling</u>	01				
Bottle Prep/Cooler Shipping	X	Rosanne A.	10/22/09	010001	4
Cooler Cleaning	X	Rosanne A.	10/22/09	010002	5
Disposal	X	Mike G./Isaak M.	01/03/04	010003	4
Log In	X	Paula S./Barb R.	10/22/09	010006	3
Sample Receiving	X	Paula S./Barb R.	10/21/09	010007	6
Thermometer Calibration	X	Mike G.	04/15/03	010008	1
Sample pH	X	Mike G.	10/22/09	010009	2

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Pipet Calibration	X	Mike G.	06/04/10	010010	2
Sterilization of Regulated Samples	X	Kara T.	05/19/10	010011	2
Safe Handling of Hazardous Materials	X	Mike G./Andy B.	08/18/09	010012	1
Sub Sampling of Solids, Waste, and Semi-Solid Materials	X	Maya M./Isaak M.	10/15/10	010013	1
<u>Field Services</u>	02				
Drum Sampling	X	Mike G.	11/26/01	020001	3
Low-level Mercury Sampling	X	Maya M./Mike G.	04/16/03	020002	1
Sample Splitting	X	Mike G.	01/02/02	020003	2
Sampling Utility Manholes	X	Mike G.	01/02/02	020004	3
Solid Sampling	X	Mike G.	01/02/02	020005	2
Wastewater Sampling	X	Mike G.	11/26/01	020006	2
Field pH	X	Mike G.	10/16/03	021501	1
Residual Chlorine Field	X	Mike G.	01/17/05	024500C	1
<u>Inorganics</u>	03				
Acidity	X	Mike C.	05/21/10	033101A	4
Alkalinities	X	Kara T.	07/20/10	033101B	3
Ammonia	X	Mike C.	07/19/10	033503	8
Available Cyanide	X	Jeff P./Barb R.	05/02/11	031677	1
Available Cyanide Preparation	X	Jeff P./Barb R.	05/02/11	031677PREP	1
BOD5/CBOD - SM5210B	X	Megan H.	07/15/10	034051	6
BOD5/CBOD - New Method	X	Kara T.	05/25/10	0310360	2
Winkler Method Modified	X	Mike G.	03/17/08	033602M	2
Carbon Dioxide	X	Mike C.	05/25/10	034500A	2
Chloride (titration)	X	Kara T.	05/21/10	033253	3
COD	X	Mike C.	06/01/10	034104	3
Conductivity	X	Kara T.	05/20/10	031201	2
Cyanide (colorimetric)	X	Jeff P.	05/09/08	033354	9
Cyanide Distillation	X	Jeff P.	05/08/08	03LACHATCN	4
Density solids	X	Kara T.	06/01/10	032710	3
Density liquids and powders	X	Kara T.	06/01/10	032710B	3
Dissolved Oxygen - New Method	X	Kara T.	06/04/10	0310360DO	2
Dissolved Sulfide Prep	X	Jeff P.	06/03/10	034500S2	2
DO Meter Calibration	X	Mike G.	05/12/10	030001	2

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Ferrous Iron	X	Jeff P.	05/27/10	03HACHA	2
Hardness	X	Kara T.	05/21/10	032340	5
Hexavalent Cr	X	Kara T./Isaak M.	03/30/05	032184	4
Hexavalent Cr Digestion	X	Jeff P./Isaak M.	07/21/03	033060	4
Ion Chromatography	X	Jeff P.	05/12/10	033000	6
MBAS	X	Mike C./Jeff P.	05/27/10	034251	3
Nitrite (colorimetric)	X	Jeff P.	01/27/06	034500B	4
Phenols	X	Jeff P.	06/02/10	034201	6
Phenols Distillation	X	Jeff P.	06/02/10	03LACHETA	3
Phosphorus	X	Mike C.	06/03/10	033652	6
Reactive Cyanide	X	Jeff P.	09/24/01	039010	1
Residual/Total Chlorine	X	Jeff P.	05/21/10	038167	3
Silica	X	Jeff P.	05/27/10	034500	3
Sulfide Analysis	X	Jeff P.	06/01/10	033762	6
Sulfide Distillation	X	Jeff P.	06/01/10	03LACHATB	3
Sulfite	X	Barb R./Jola B.	06/01/10	030004	1
TKN	X	Mike C.	06/01/10	033514	7
TOC	X	Jeff P.	01/29/02	034151	2
Turbidity	X	Kara T.	06/01/10	03HACH	2
pH (Liquid)	X	Mike G.	06/01/10	031501	6
pH (Solid)	X	Joesph K.	06/01/10	039045D	2
Specific Gravity by Hydrometer	X	Kara T.	06/01/10	03D891	2
Total Dissolved Solids	X	Mike G.	05/25/10	031601	5
Total Solids/Total Volatile Solids/Ash	X	Mike G.	06/02/10	031603	6
Total Suspended Solids/ Volatile Suspended Solids	X	Mike G.	06/02/10	031602	5
Total Solids in Water	X	Mike G.	06/02/10	031603B	6
Viscosity	X	Kara T.	06/01/10	034212	2
FOC by Walkley Black	X	Jeff P. / Andy B.	05/27/10	030002	2
Determination of H2O2 with KMnO4	X	Mike G./Andy B.	12/14/09	030003	1
<u>Extractions</u>	04				
BNA/Herbs (soil)	X	Steve P./Andy H.	03/03/06	043550B	5
MBAS	X	Jola B./Kara T.	01/26/04	044251	2
Oil & Grease (Freon, Grav.)	X	Ken M.	05/08/02	044131A	1
Oil & Grease (Hexane, Grav.)	X	Ken M.	07/16/10	041664A	4

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Oil & Grease Soxhlet	X	Chris D.	07/15/03	049071	1
Oily Waste Extraction	X	Troy S.	06/21/07	041330A	1
PCB (water)	X	Brent W./Ken M.	12/12/06	043510	9
PCB (soil)	X	Brent W./Ken M.	12/12/06	043550	8
PNA/BNA/TCLP	X	Brent W./Ken M.	03/03/06	043510C	6
PCB-Silica Gel Clean-Up	X	Troy S.	03/06/06	043630C	1
TPH (Hexane, Grav.)	X	Ken M.	05/08/02	041664B	1
<u>TCLP/Waste Analyses</u>	05				
%Oil and % Water	X	Andy H.	04/21/10	059688	2
BTU and Total Halogens	X	Kara T.	06/04/10	055050	2
Flash Point for liquids	X	Kara T.	05/11/10	05D3278	2
Flash Point for solids	X	Kara T./Andy H.	05/25/10	051030	2
Paint Filter Test	X	Mike G.	06/02/10	059095	2
SPLP Extraction	X	Andy H./Isaiah M.	06/03/10	050608	2
TCLP Extraction	X	Andy H./Isaiah M.	06/04/10	051311	7
<u>Sample Preparation</u>	06				
Analysis Calculations	X	Steve P.	10/26/09	060001	2
Batch Number Tracking	X	Steve P.	06/06/02	060002	1
Glassware Washing	X	Mike G.	05/19/10	060003	2
Method Detection Limits	X	Steve P.	10/23/09	060004	5
Scale/Weight Calibration	X	Mike G.	10/27/09	060005	3
Significant Digits	X	Steve P./Maya M.	01/04/02	060006	1
<u>Organics</u>	07				
5035 Prep.	X	Josh H.	11/11/10	075035	5
5035 Prep. - VAP	X	Megan H./Josh H.	10/09/06	075035-VAP	3
PCBs by GC (Method 608)	X	Janusz B./Maya M.	06/01/04	070608	1
PCBs	X	Janusz B./Maya M.	04/29/08	078082	10
Pests	X	Janusz B. /Joe K.	06/01/10	078081	3
Peak Integration	X	Steve P.	01/05/07	070001	3
SVOCs/DRO	X	Steve P./Brent W.	11/04/10	078270	10
VOCs/GRO	X	Josh H./Steve P.	06/03/10	078260	11

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VOCs/GRO - VAP	X	Josh H./Steve P.	03/25/08	078260-VAP	10
Drinking Water VOCs	X	Josh H./Andy B.	06/03/10	075242	2
<u>Metals</u>	08				
Digestion (Liquid)	X	Emil B.	09/27/10	083015	7
Digestion (Liquid) - VAP	X	Andy B./Sarah S.	10/01/10	083015-VAP	6
Digestion (Soil)	X	Emil B.	09/27/10	083050B	8
Digestion (Soil) - VAP	X	Andy B./Sarah S.	10/04/10	083050B-VAP	7
Hg (Digestion & Analysis)	X	Emil B.	05/18/08	087470	8
Hg Drinking Water	X	Emil B.	02/01/11	082451	10
ICPMS 6020A	X	Andy B./Barb R	01/12/11	086020A	1
ICPMS 6020A - VAP	X	Andy B./Barb R	07/15/10	086020A-VAP	1
<u>Maintenance</u>	09				
Emergency Showers		Eugene B. Mike G.	01/22/03		
General Maintenance		Eugene B. Mike G.	01/22/03		
Hood Airflow		Eugene B. Mike G.	01/22/03		
Reagent Handling		Eugene B. Mike G.	01/22/03		
Refrigerator	X	Barb R. Andy B.	03/26/10	090001	1
Water Purity (DI)	X	Mike G. Barb R.	03/26/10	090002	1